expressed doubt that the line was due to free manganese. It is clear from the present data, of course, that free manganese cannot be responsible since the Mn curve shows no line absorption at low energies. In addition, only a negligible reduction of $KMnO_4$ could occur during a single run in our experiments.

A single absorption line has the form[5]

$$\mu(\nu)=\frac{A}{(\nu-\nu_0)^2+(\Gamma/2)^2},$$

where Γ is the width at half-maximum, and $(\nu-\nu_0)$ is the distance from the center of the line. The entire long wave-length side of the peak can be matched almost perfectly with a curve which sets $\Gamma=2.2$ ev with no correction for the 1, -1 rocking curve width. When the correction is made, one finds that the width agrees reasonably well with that obtained from the manganese metal edge.

It is difficult to see why this strong, narrow level should occur where it does. Two possible explanations can be discussed.

First, since the bonding in the complex is homopolar in nature, one might suspect that, through the hybridization of orbitals, a low lying level is formed to which the 1*s* electron is permitted to go. The bonding[9] in the MnO_4 tetrahedron has been suggested as a combination of sp^3 and sd^3 orbitals. This would leave a certain amount of empty 4*p* orbital which, if the Mn is neutral or near neutral in the complex, would give an absorption near the observed white line. On this explanation one can account for the less intense white line absorption in K_2MnO_4 than in $KMnO_4$ since the extra electron of K_2MnO_4 probably fills up some of the levels causing the line absorption.

A second, less convincing, explanation is that the white line is due to constructive interference between a directly emitted electron wave and the wave scattered from neighboring atoms. This point of view, first proposed by Kronig,[13] correctly predicts the positions of several sharp absorption lines which have been observed[14] in the Ge K edge in $GeCl_4$ vapor, and the As edge in $AsCl_3$. However, it seems quite incorrect to apply Kronig's theory to the lowest energy absorption in an edge since in such an excited state the electron probably remains bound to the absorbing molecule.

The Mn in $KMnO_4$ may be formally considered to have a valence of 7, and one observes that the main edge is found at considerably higher energies than the 4*p* peak in the ionic compounds. The main edge in K_2MnO_4, where the formal valence is 6, is found at somewhat lower values than in $KMnO_4$. These shifts probably have nothing to do with the formal valence as was formerly considered to be the case, and the explanation lies in the influence that the homopolar bonding has on the energy levels.

5. MnO_2 and MnS

Absorption into low lying levels is also observed in MnO_2 and MnS. The absorption due to free manganese suggests itself as an explanation of the effect, but it can be discounted, at least in MnO_2, for the reason discussed under $KMnO_4$, namely, there exists a region of negative slope in the MnO_2 curve near 2 or 3 ev which is not present in the Mn curve. The explanation must lie in the partial homopolar nature of the bond.

The MnS edge is quite similar in general appearance to the edges observed by Yoshida[2] for the sulfides of iron. Since the shape of the edge is so unlike those obtained for the ordinary ionic compounds of manganese, it seems quite certain that the binding in MnS is predominantly homopolar in nature. This is in keeping with the relatively low position of sulfur on the electro-negativity scale.

The results may be summarized by the general statement that the amount of absorption into levels in the 3*d* range increases with the amount of electron sharing.

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[13] R. de L. Kronig, Zeits. f. Physik **75**, 468 (1932).

[14] S. T. Stephenson, Phys. Rev. **71**, 84 (1947).

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Pressure Broadening in the Inversion Spectrum of Ammonia

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A formula is developed to explain the low pressure line widths observed in the inversion spectrum of NH_3 by Bleaney and Penrose. The assumptions made are those characteristic of the *statistical* theory of pressure broadening. The result, which is entirely devoid of adjustable parameters, agrees with the data about as well as do the impact theories with their unreasonable collision radius.

THE development of high precision techniques in microwave spectroscopy offers new and attractive opportunities for solving the old problem of the broadening of spectral lines. This problem had never received a complete and wholly satisfactory treatment, and the excitement over new events in the realm of the nucleus

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quickly drained it of interest and of attention. Now interest is shifting back and seeking its former focus. The present note, if it makes any contribution at all, is merely to aid in this process of focusing thought upon crucial issues. The circumstance that the simple theory here developed accounts for the facts is, after all, perhaps fortuitous.

There are two fundamental approaches to the theoretical study of pressure broadening. The first, and older, was initiated by Lorentz and results in a concept known as *collision broadening* or *impact broadening*.[1] Impact theory starts from the classical idea that interruptions of a continuous absorption or emission process produce a frequency spread of the absorbed or emitted radiation, and the spread is proportional to the number of interruptions per unit time. Precisely what is meant by an interruption is, of course, not clear and it is necessary to define a suitable "shield" around a radiating molecule, whose piercing by an intruder constitutes by *fiat* a collision, that is, an interruption of the radiative process. In some instances the radius of this shield does not differ much from the gas-kinetic diameter of the molecules, but in general it is a good deal larger. And its size seems to depend on the range of the intermolecular forces. Impact theories are thus forced to operate with an undetermined, and therefore adjustable, parameter, the collision radius, which despite its intuitive appeal has no true physical significance.

The second approach to the problem is through a *statistical theory* which envisions an idealized process known as statistical broadening.[2] Based on the simplest notions of quantum theory, it conceives of the levels of a given molecule as slightly altering their positions under the influence of approaching perturbers, after the fashion of the Stark and Zeeman effects. A spectral line arising from a transition between any two levels will therefore have its frequency diffused over an interval corresponding to the range of perturbation (by intermolecular forces) of the levels concerned. The intensity within the line between ν and $\nu+d\nu$ is thus proportional to the probability, in a simple statistical sense, that the energy difference of the levels shall lie between $h\nu$ and $h(\nu+d\nu)$, and this probability is equal to the relative size of that part of configuration space for all the molecules in which the energy difference falls within the specified range.

When this probability is computed, no undetermined or adjustable parameter haunts the scene. The theory thus exposes itself to a severer test than the impact formulas and is likely to be more instructive. But it is nevertheless an extreme approach valid under special circumstances; for it is certainly true that broadening occurs as a result of the cessation of absorption (or radiation) at impact even if no distortion of the energy level scheme took place. Ultimately the two approaches must be combined; but that is not the purpose of this paper.†

Bleaney and Penrose[3] have provided a valuable set of data on the breadth of the lines of the inversion doublet in ammonia. The interesting aspect in their results is that each measured line corresponds to a single set of quantum numbers, J, K, of the absorbing molecule. This, together with the fact that these authors conducted their measurements at very low pressures, permits the formulation of a simple statistical theory which should do at least qualitative justice to their measurements.

Following recent trends, Bleaney and Penrose[4] themselves have presented an impact theory which, when casually inspected, renders good account of their results. It bears, of course, the fault of all such theories in being forced to assume an arbitrary collision radius or, what amounts to the same thing, an energy of interaction which, when exceeded, makes the approach of a second molecule count as a collision. Unfortunately, this minimum energy of interaction turns out to be about twice the separation of the inversion-doublet levels. If this were to be interpreted literally it would imply that the molecule could go on absorbing even when the perturbation is larger than its natural frequency, or indeed when the natural frequency is negative. In suggesting this, the impact theory rather defeats itself.

Bleaney and Penrose use a process for averaging over the orientations of the molecular dipoles which can be improved. In the introduction to his dissertation[5] D. F. Smith has recomputed the line widths in the fashion of these authors, but with the use of a quantum mechanical method[6] for averaging. His theoretical results fit the data as well as does these authors' curve, and he finds that a minimum energy of perturbation equal to the separation of the levels is needed to obtain numerical agreement. This relieves to some extent the internal difficulties of the impact theory, but it does not inspire confidence. We turn, therefore, to its competitor, the statistical theory.

The intermolecular forces between symmetrical top molecules carrying an electric dipole along their figure axis were calculated by D. T. Warren and the present author.[6] They showed that, at large distances of separation (corresponding to the low pressures used in the experiments here under discussion) only first-order forces proportional to $1/R^4$ are of importance; R is the

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[1] H A Lorentz, Proc. Amst. Acad. 8, 591 (1906); V. F. Weisskopf, Zeits. f. Physik 75, 287 (1932); J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. 17, 227, 1945. Both types of theory are reviewed in some detail by W. W. Watson and the author in Rev. Mod. Phys. 8, 22 (1936).

[2] H. Margenau, Phys. Rev. 40, 387 (1932); 48, 755 (1935); E. Lindholm, Arkiv för Mat., Astr. och Fysik 28, 1 (1941); 32, 1 (1945); H. M. Foley, Phys. Rev. 69, 616 (1946)

† *Note added in proof.*—A significant study of this problem has been made by *P. Anderson*, whose paper, now in process of publication, came to the author's attention after the present note was submitted.

[3] B. Bleaney and R. P. Penrose, Proc. Roy. Soc. A189, 358 (1947).

[4] B. Bleaney, Physica 12, 595 (1946); also C. V. D. Report CL. Misc. 70 (1948).

[5] De Forest F. Smith, Dissertation, Yale University, 1948.

[6] H Margenau and D. T. Warren, Phys. Rev. 51, 748 (1937).

distance between the centers of two interacting molecules. Indeed if one molecule is in the state described by the quantum numbers J and K, the other in the state J', K', and both carry a dipole moment μ, then the energy of interaction, which depends on these four quantum numbers and upon a fifth, λ, (to be discussed presently), may be written

$$V(J, K, J', K', \lambda)=\frac{\mu^2}{R^3}\frac{KK'}{J(J+1)J'(J'+1)}\epsilon_\lambda. \quad (1)$$

The individual M's of the two molecules are not "good quantum numbers," since the separate angular momenta about the intermolecular axis are not conserved. But there are as many quantized states of interaction as there are values M, M', that is, $(2J+1)\cdot(2J'+1)$ states. These are labeled by the index λ, and ϵ_λ is a numerical factor for each of these states. Now the mean value of V for a given set J, K, J', K' vanishes,[6]

$$\sum_\lambda \epsilon_\lambda=0. \quad (2)$$

Hence there is no mean displacement, no shift of the spectral line.

The numbers ϵ_λ are in general irrational and can only be computed as roots of a secular determinant. But their values will not be needed here.

If $E(J, K)$ is the normal energy of separation of the doublet levels, the frequency of a line absorbed by one ammonia molecule (JK) when another (J', K') is a distance R away will be

$$\begin{aligned}\nu=h^{-1}[E(J, K)+V(J, K, J', K', \lambda)\\ -V(J, K, J', K', \mu)],\\ =\nu_0+B_{\lambda\mu}/R^3\end{aligned}$$

provided we put

$$B_{\lambda\mu}=\frac{\mu^2}{h}\frac{KK'}{J(J+1)J'(J'+1)}(\epsilon_\lambda-\epsilon_\mu)=b(\epsilon_\lambda-\epsilon_\mu). \quad (3)$$

This is true because in passing from one to the other of the inversion states the dipole merely alters its orientation, which means that the perturbation V changes from one permitted state λ to another, μ. There will, of course, be selection rules, but we shall ignore them in view of the fact that the number of possibilities for λ and μ is fairly large even for moderate J and J'.[7] We shall assume the ϵ_λ to have a random distribution; to ignore the selection rules is then tantamount to supposing that the levels μ which can be reached from a level λ are still distributed at random.

Henceforth we write a single subscript, σ, for the pair λ, μ and understand that σ runs from 1 to n where $n=[(2J+1)(2J'+1)]^2$.

Consider now an absorbing molecule as it moves through the gas. The theory to be developed is the simplest possible one, constructed on the premise that all collisions are *binary* encounters. This limits its validity to low pressures. On this basis one may think of an absorber as moving, successively, through the "private" spaces of all perturbers, each of which has a volume N^{-1} if there are N molecules per cc. For statistical purposes we select n such private spaces, one for each type of interaction $(1\leqslant\sigma\leqslant n)$. In the σth space or cell, $\nu=\nu_0+B_\sigma/R^3$, or

$$f=B_\sigma/R^3, \quad (4)$$

if f is the frequency measured from the center of a broadened line. The portion of the σth space (which may be considered spherical) wherein the frequency lies near f is a spherical shell of radius R such that R satisfies Eq. (4). In other words, the probability for this particular value of f contributed by cell σ is

$$I_\sigma(f)df\propto(4\pi/3)(dR^3/df)_\sigma df. \quad (5)$$

If $f>0$, only one-half of the n cells can contribute to the probability, for half the perturbations, i.e., half the B_σ, are negative. The intensity of the line at f is therefore obtained by summing (5) over the $n/2$ values of B_σ that are positive:

$$I(f)=\left|\frac{N}{n}\sum_\sigma^{n/2}\frac{4\pi}{3}\left(\frac{dR^3}{df}\right)_\sigma\right|=\frac{4\pi}{3}\frac{N}{n}\left|\sum_\sigma^{n/2}\frac{d}{df}\left(\frac{B_\sigma}{f}\right)\right|$$

in view of Eq. (4). The factor N/n is the reciprocal of the volume of all available cells. The distribution of the B_σ is symmetric about the value zero (see Eq. (2)), and the last sum may be replaced by

$$\frac{1}{2}\frac{d}{df}\sum_\sigma^n\frac{|B_\sigma|}{f}.$$

We thus obtain

$$I(f)=\frac{2\pi}{3}\frac{N}{f^2}\frac{\sum_\sigma|B_\sigma|}{n}. \quad (6)$$

A word must be said about the normalization of I. In cell σ, the smallest value of f is not zero but $B_\sigma/R_{\mathrm{max}}{}^3$ and $R_{\mathrm{max}}{}^3=3/4\pi N$. In computing $\int Idf$, the lower limit must be taken to be different in every term of the

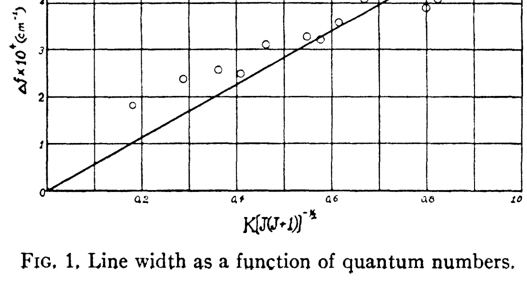

FIG. 1. Line width as a function of quantum numbers.

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[7] Perhaps it is significant that the lines for which J is lowest (2 and 3) show the widest departures from our theoretical curve.

summation, namely $(4\pi/3)NB_\sigma$ in the term σ, while the upper limit is always ∞. With that understanding,

$$\int I(f)df=\tfrac{1}{2}$$

as it should be for the positive half of the f-distribution. *In toto*, then, $I(f)$ is normalized to 1.

In evaluating the sum of Eq. (6) it is necessary to assume a Gaussian distribution for the B_σ. This is doubtless a good approximation, for the value of n is quite large. The reader will note, of course, that this is not the same as a replacement of the spectral line by a Gauss curve. This latter procedure is wholly unjustified because a Gauss curve has a finite standard deviation whereas a spectral line (dispersion curve) does not. For a Gaussian distribution the mean of the absolute values is $(2/\pi)^{\frac{1}{2}}$ times the standard deviation; therefore

$$1/n\sum_\sigma |B_\sigma| = (2/\pi)^{\frac{1}{2}}[n^{-1}\sum_\sigma B_\sigma{}^2]^{\frac{1}{2}}. \tag{7}$$

We now recall that $B_\sigma = b(\epsilon_\lambda - \epsilon_\mu)$, and

$$\sum_\sigma B_\sigma{}^2 = b^2\sum_{\lambda\mu}(\epsilon_\lambda-\epsilon_\mu)^2 = 2b^2n^{\frac{1}{2}}\sum_\lambda \epsilon_\lambda{}^2 = 2b^2n\epsilon^2.$$

The mean square energy ϵ^2 was calculated in reference 6; it is

$$\epsilon^2=\tfrac{2}{3}J(J+1)J'(J'+1).$$

On inserting it, and on putting Eq. (7) back into Eq. (6), we have

$$I(f)=\frac{4}{3}\left(\frac{2\pi}{3}\right)^{\frac{1}{2}}\frac{\mu^2}{h}\frac{KK'}{[J(J+1)J'(J'+1)]^{\frac{1}{2}}}\frac{N}{f^2}. \tag{8}$$

This result is correct only for values of f that are larger than the minimum perturbations occurring in the various cells. Experiment shows pressure broadened lines to have in fact an asymptotic distribution proportional to f^{-2}, for they conform to the dispersion law

$$I(f)=1/\pi[\Delta f/(f^2+(\Delta f)^2], \tag{9}$$

which approaches

$$I(f)\rightarrow 1/\pi(\Delta f/f^2), \tag{9'}$$

for large f.

To derive a formula of the dispersion type one would have to treat the lower limits of f in the different cells with more care than we have done; but this is not necessary for the present purpose.

Equation (1) represents a contour that is also normalized to 1, and Δf, sometimes called the half-half-width, is the distance on either side from $I_{\max}$ at which I has the value $\frac{1}{2}I_{\max}$; it is the quantity plotted in the diagrams of Bleaney and Penrose. Upon comparing (8) with (9′) we conclude

$$\Delta f=2\left(\frac{2\pi}{3}\right)^{\frac{3}{2}}\frac{\mu^2}{h}N\frac{KK'}{[J(J+1)J'(J'+1)]^{\frac{1}{2}}}. \tag{10}$$

There remains only the task of averaging over the values of K' and J' which characterize the states of the molecules perturbing the absorber. This computation must be carried out with the proper weighting factors.

$$\{K'[J'(J'+1)]^{-\frac{1}{2}}\}_{\text{Av}} = \frac{\sum_{J'K'} K'(J'^2+J)^{-\frac{1}{2}}g(J',K')\exp[-W(J'K')/kT]}{\sum_{J'K'} g(J',K')\exp[-W(J',K')/kT]}.$$

The sums were evaluated by D. F. Smith;[5] the average is 0.54 for a temperature of 20°C. The dipole moment $\mu=1.44\times10^{-18}$ e.s.u. for ammonia. This leads to the final result

$$\Delta f/p=1.13\times10^{-3}[K^2/J(J+1)]^{\frac{1}{2}} \times(\text{cm}^{-1}/\text{mm Hg})\text{ at }20^\circ\text{C}. \tag{11}$$

Here the pressure p, as indicated, is in mm of mercury. The measurements of reference 3 were made at $p=0.5$ mm. They are plotted in Fig. 1, the straight line representing Eq. (11). Agreement between Bleaney and Penrose's data and the present theory is perhaps not quite as good as that obtained by the authors themselves, but it seems nevertheless significant.

To understand line width data at higher pressures of the absorbing gas an extension of statistical theory beyond this simple stage is required, for it is certain that impact theory can lay no claim to conceptual adequacy when the mean perturbation is as great as the distance between the undisplaced energy levels, which is true at atmospheric pressure in ammonia. Theoretical progress is then impeded largely by three obstacles.

First, the forces between the dipole molecules are not additive, and it appears very difficult to calculate the aggregate effect of many cooperating encounters. The problems that beset the theory of condensation of a dipole gas raise their heads at this point.

Second, forces of shorter range than those here considered must be included in the calculation for higher pressures. These forces are not attractive and repulsive with equal probabilities. When they become important a shift of the line should be observed.

Finally, the whole picture of an absorbing ammonia molecule in the neighborhood of perturbing molecules will break down. The level separation in the inversion spectrum results from the existence of a potential hill through which the N-atom must pass to reach the inverted position. That separation may be lessened on sufficiently close approach of a dipole. Qualitative considerations indicate that it should be diminished by interactions, a fact quite in line with recent findings[8, 9] which seem to require a decreasing "natural" frequency as the pressure increases. But this is an effect that will be checked by more careful calculation.

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[8] De Forest Smith, Phys. Rev. 74, 506 (1948).

[9] I. R. Weingarten, Columbia Rad. Lab. Report, May 1, 1948.