771.5, 771.9, 772.4, 772.9, 773.0), 780 Å (lines O IV 779.8, 779.9, and a weak unidentified line at 779.0), and 790 Å (lines O IV 787.7, 790.1, 790.2, and weak unidentified lines at 786.8, 789.3). On the ordinate is plotted the collected electron current per unit light intensity. Corrections have been made for scattered light and background gas. The retarding potential is plotted on the abscissa. At zero retarding potential, the height of each curve should be proportional to the ionization cross section. It is clear that some process which may be assumed to be autoionization has made the cross section at 780 Å much larger than it is at 772 or 790 Å. The light-source lines at 780 Å appear to lie at a wavelength which is on the shoulder of an autoionization peak shown in the work of Cook and Metzger[5] and Diebler, Reese, and Krauss.[6] The arrows on the figure mark the calculated appearance potentials of the vibrational states of H_2^+ (no account of rotational structure was taken). Double arrows are used at 790 Å to illustrate the energy spread among the several lines within the bandwidth. Any vibrational excitation of H_2^+ molecule ions should have been reflected in a decrease in the energy of the ejected electrons. Thus, as the retarding potential is decreased at any particular wavelength of exciting radiation, a rise in the current per unit light intensity should be noted at the appearance potential of each vibrational state excited. As shown in the figure, such rises are noted, the vibrational states have been resolved, and a strong enhancement of the excitation of the $v = 1$ state has taken place at 780 Å, but not at 772 Å. It is assumed that at 780 Å the $v = 1$ state was excited largely through autoionization. The $v = 0$ state could have been excited directly.

In the case of hydrogen the autoionization comes only from vibrationally excited states of highly excited electronic configurations of H_2. In other molecules, however, the possibility exists of producing autoionization from electronic configurations with no vibrational excitation. In some of these cases, also, a change in the vibrational-state distribution from that of the directly excited ion may be expected on the basis of different internuclear separations in the autoionizing state and in the ion. This possibility has been pointed out in the electron-retarding results from CO.[4] It would appear to be possible in O_2[2] and should be sought in other molecules, also.

The authors wish to acknowledge the aid of the staff of the Boeing Scientific Research Laboratories and to thank Dr. T. Namioka of the U. S. Air Force Cambridge Research Laboratory for a stimulating correspondence. We are grateful to Dr. H. Rosenstock for calling our attention to the work of Dr. Dibeler and his associates and to Dr. Dibeler and Dr. Cook for allowing us to see preprints of their work.

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TRANSITION FROM RESONANT TO NONRESONANT LINE SHAPE IN MICROWAVE ABSORPTION

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(Received 20 January 1965)

This Letter presents a new expression for the variation with pressure of the spectral intensity distribution in microwave absorption lines of gases, with specific application to the ammonia inversion spectrum. Earlier attempts to apply the prevailing Van Vleck–Weisskopf[1] (VVW) line shape expression has only a partial success, and only at the price of regarding the resonance frequency and the linewidth as freely adjustable functions of pressure. Most notable is the behavior of the ammonia inversion spectrum under pressure,[2,3] which is seen to shift gradually from the resonant (VVW) to the nonresonant (Debye) line shape as the pressure is increased, with an accompanying reduction of the collision cross section.

The expression presented here follows from the existing line shape theory first expounded by Baranger[4] and re-established by Fano[5] from the point of view of relaxation theory. In Fano's terminology, each line in the spectrum is associated with an eigenstate of the Liouville representation: The initial (i) and final (f) levels of the absorption line form together the eigenstates $|if\rangle$ of the Liouville operator L_0, whose eigenvalues are the resonance frequencies ω_{if}. The effect of collisions, statistically averaged, is to introduce a time-independent non-Hermitian perturbation[6] Λ to the single-molecule operator L_0. Its diagonal matrix elements give rise to the shift and width of isolated lines of the kind discussed by Anderson,[7] whereas the nondiagonal elements describe the coupling of lines by inelastic collisions.[4]

The Liouville representation, though apparently more complex than the conventional Hamiltonian representation, has a more direct appeal to our experience (since lines and not energy levels are observed by spectroscopists) and to our intuition (since its eigenstates correspond to the "oscillators" of the classical theory).

A peculiar property of L_0 is that to each eigenstate $|if\rangle$, with positive frequency ω_{if}, corresponds an eigenstate $|fi\rangle$, with negative frequency $\omega_{fi} = -\omega_{if}$, which will also give rise to absorption when sufficiently broadened by collisions. This absorption is represented by the "negative resonance" terms in the VVW expression.

The derivation of the new expression is based on the realization that the positive and negative eigenvalues are coupled by inelastic collisions, just as any two distinct positive eigenvalues.

Consider a single, nondegenerate dipole-radiation line[8] and the corresponding pair of eigenvalues of L_0 ($\pm\nu_0$ in wave numbers). Supposing Baranger's impact approximation is valid, the coupling between these eigenvalues is represented by a single real parameter ζ which, like the shift δ and the width γ, is proportional to the gas density. This parameter (ζ) is, in essence, the rate of inelastic collisions that cause transitions between the initial and the final states of the line. Neglecting coupling with other resonances,[9] the relevant perturbed Liouville matrix reduces simply to

$$L_0 + \Lambda = \begin{pmatrix} \nu_0 + \delta - i\gamma & i\zeta \\ i\zeta & -\nu_0 - \delta - i\gamma \end{pmatrix}. \qquad (1)$$

The absorption coefficient for a microwave line ($\hbar\omega \ll kT$) is then found to be

$$\alpha(\nu) = (4\pi^2 N/3kT)\rho_i |\mu_{if}|^2 \nu^2 F(\nu), \qquad (2)$$

with the "shape factor"

$$F(\nu) = \frac{2(\gamma-\zeta)\nu^2 + 2(\gamma+\zeta)[(\nu_0+\delta)^2 + \gamma^2 - \zeta^2]}{[\nu^2 - (\nu_0+\delta)^2 - \gamma^2 + \zeta^2]^2 + 4\nu^2\gamma^2}, \qquad (3)$$

where all frequencies are expressed in wave numbers. In case the coupling coefficient ζ is negligible, Eq. (3) turns into the familiar VVW expression

$$F_{\mathrm{VVW}}(\nu) = \frac{\gamma}{(\nu-\nu_0-\delta)^2 + \gamma^2} + \frac{\gamma}{(\nu+\nu_0+\delta)^2 + \gamma^2}. \qquad (4)$$

On the other hand, when the resonance frequency $\nu_0 + \delta$ becomes negligible, Eq. (3) takes the nonresonant (Debye) line shape

$$F_D(\nu) = 2(\gamma-\zeta)[\nu^2 + (\gamma-\zeta)^2]^{-1} \qquad (5)$$

with a reduced width $\gamma - \zeta$.

Figure 1 shows the fit of Eq. (3) to the NH_3 inversion data[2] at six different pressures, using the resonance frequency $\nu_0 = 0.78\ \mathrm{cm}^{-1}$ and

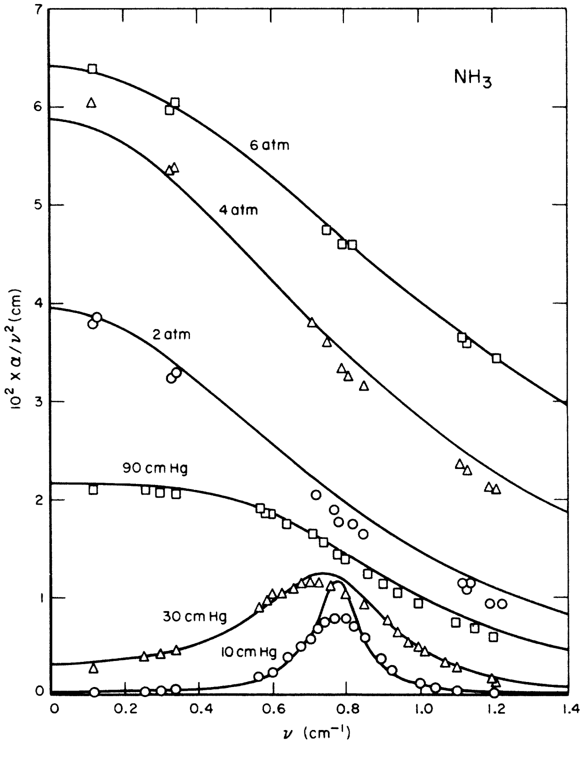

FIG. 1. Ammonia inversion spectrum—comparison of theoretical line shape, Eq. (3) (solid lines), with the measurements of Bleaney and Loubser[2] at various pressures.

the total intensity factor $(4\pi^2 N/3kT)\sum_{if}\rho_i|\mu_{if}|^2 = 6.85\times10^{-3}\times p$ (where p is the pressure in atmospheres), with the three parameters

$$\gamma/p = 0.58\ \mathrm{cm}^{-1}/\mathrm{atm},\quad \zeta/p = 0.38\ \mathrm{cm}^{-1}/\mathrm{atm},$$
$$\delta/p = -0.015\ \mathrm{cm}^{-1}/\mathrm{atm},$$

determined by trial and error (no least-square-deviation adjustment was attempted).

This figure shows that the single-line ex-pression is inadequate at low pressures (below ~$\frac{1}{2}$ atm) where the finite spread of frequencies in the inversion band, composed of many lines, is still comparable to the pressure broadening. However it can be shown that, with increasing pressure, the broadening and coupling of the lines will make the band profile approach the shape resulting from a single resonance line.

Equation (3) is still valid, even with very low pressures, far out in the wings of the band. But there too it shows a significant departure from the VVW line shape. The absorption, in the limit of low pressure, is proportional to $p(\gamma+\zeta)$ near $\nu = 0$, and to $p(\gamma-\zeta)$ at $\nu \gg \nu_0$, whereas with the VVW expression it would be proportional to $p\gamma$ in both wings. This may account for the considerable departure from the VVW expression observed in the low-frequency wing of ammonia.[10] Using Eq. (3), with the parameters given here, the value of α/ν^2 calculated for NH_3 at $\nu = 0.094\ \mathrm{cm}^{-1}$, $p = 10$ cm Hg, is 3.86×10^{-4} cm, compared with an experimental value of $(3.7\pm0.2)\times10^{-4}$ at a temperature $T = 288°\mathrm{K}$. There is some evidence of the existence of similar effects in both wings of ND_3 and in the low-frequency wings of the rotational spectra of COS and N_2O.[11]

The value of γ used in Fig. 1 (0.58) is significantly lower than the average width (0.62) derived from the low-pressure data.[2] Such a difference is expected owing to the coupling of the various inversion lines. The value of the band shift δ is inconclusive since, being so small, the line shape is only slightly sensitive to its variation. It has, anyhow, the order of magnitude of the shifts of constituent lines reported by various observers.[12]

A behavior similar to that of ammonia has been observed in the magnetic-dipole spectrum of oxygen.[13] Its analysis is complicated by the existence of a nonresonant (zero-frequency) spectrum at low pressures, in addition to resonant absorption.

A more detailed exposition of the theory and its interpretation, with further implications for the microwave spectra of ammonia and other gases, will be presented in future publications. These will include discussions of the validity of the Van Vleck-Weisskopf expression, the coalescence of a group of lines under pressure, nonresonant absorption by symmetric-top molecules, and saturation phenomena.

The author wishes to acknowledge his gratitude to Dr. A. A. Maryott for presenting the problem to him and for supplying him with the relevant data. Thanks are also due to Dr. U. Fano for his continued interest, and to Dr. L. Frenkel and Dr. R. Zwanzig for helpful discussions.

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