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Collision and Saturation Broadening in Microwave Spectra*

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A theory of spectral line shape is presented for the case of a low pressure gas where only two energy levels (or several pairs of independent levels) are active in producing absorption. In Section I, an approximate set of differential equations is derived; these are solved in Section II. The method of approximation is shown to be consistent in Section III, and the final results are obtained in Section IV. A definite broadening of the lines in addition to that due to molecular collision is predicted as saturation is approached. The incident power needed for a given effect is proportional to the square of the pressure, and the maximum attenuation factor multiplied by the square of the half-width should be independent of incident power.

INTRODUCTION

IN spectroscopic work, it is generally appreciated that, owing to the limited population of states, a given amount of material can absorb no more than a certain maximum power independent of the electromagnetic power incident on the sample. Recent work in the microwave region has made it possible to reach values of incident flux sufficiently high to exhibit saturation effects. There has been some discrepancy[1–3] as to whether this saturation is accompanied by a broadening of the resonance absorption over and above that due to molecular collision alone. We shall present below a theory of spectral line shape which, it will be seen, definitely predicts additional broadening due specifically to saturation.

This theory is based on the following assumptions. The phenomena involved have three important characteristic times: the duration of a molecular collision T, the period of the incident radiation $1/\omega$, and the mean time between collisions τ. (a) It will be assumed that $T \ll 1/\omega \ll \tau$. (b) Only two energy levels are active in producing absorption. (c) Molecular collision restores a Boltzmann population.

Assumption (b) can be slightly relaxed to the extent that no energy level shall make a transition to more than one other level. In this latter case, the absorptions produced by the independent pairs of active levels can safely be added to give the total effect of the several lines. The results, however, must be expected to hold only in the near vicinity of a single line or group of independent lines.

Assumption (c) essentially states that the effects of molecular collision are to be independent of the presence of the electromagnetic field. A collision is to be regarded as a "violent" event compared to the action of the field.

Assumption (a) implies that the pressure must be low. In particular, the collision diameter must be negligible compared to the mean free path.

SECTION I

For any assemblage of quantum-mechanical systems, the density matrix, ρ, satisfies the following differential equation (superior dots indicate differentiation with respect to time).

$$i\hbar\dot{\rho} = [H, \rho]. \tag{1}$$

In our problem, the Hamiltonian matrix H is given by

$$H = H_0 + V\sin\omega t, \tag{2}$$

where the field-free Hamiltonian H_0 and the parameter V are independent of t. Choosing a representation in which H_0 is diagonal and letting

$$\rho_{nm} = e^{-i\omega_{nm}t}c_{nm}; \quad \omega_{nm} = (E_n{}^0 - E_m{}^0)/\hbar,$$

we obtain from (1):

$$i\hbar\dot{c}_{nm} = \sin\omega t \sum_l (V_{nl}e^{i\omega_{nl}t}c_{lm} - c_{nl}V_{lm}e^{i\omega_{lm}t}).$$

In accordance with the "two-level" assumption (b) above, we shall retain in these equations

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[1] C. H. Townes, Phys. Rev. 70, 665 (1946).

[2] W. V. Smith and R. L. Carter, Phys. Rev. 72, 638 (1947).

[3] T. A. Pond and W. F. Cannon, Phys. Rev. 72, 1121 (1947).

only the terms involving c_{11}, c_{12}, c_{21}, c_{22}. If several independent pairs of levels are active, we obtain corresponding sets of equations for each pair; these sets can be independently treated by the method used below. With the definition

$$D=c_{22}-c_{11}=\rho_{22}-\rho_{11}, \tag{3}$$

these equations become:

$$\begin{aligned} i\hbar\dot{D}&=2\sin\omega t[V_{21}e^{i\omega_{21}t}c_{12}-c_{21}V_{12}e^{i\omega_{12}t}],\\ i\hbar\dot{c}_{12}&=\sin\omega t[V_{12}e^{i\omega_{12}t}D+c_{12}(V_{11}-V_{22})], \qquad (4)\\ i\hbar\dot{c}_{21}&=-\sin\omega t[V_{21}e^{i\omega_{21}t}D+c_{21}(V_{11}-V_{22})]. \end{aligned}$$

In view of assumption (a) above, we shall neglect rapidly varying terms inasmuch as their effects might be expected to be practically self-cancelling over the comparatively long time periods between collisions. We shall see in Section III that this approximation can be shown to be consistent. Writing $\sin\omega t$ in complex form and retaining only slowly varying parts, we obtain finally

$$\dot{D}=-(1/\hbar)[V_{12}c_{21}e^{i\delta t}+V_{21}c_{12}e^{-i\delta t}], \tag{5a}$$

$$\dot{c}_{12}=(1/2\hbar)V_{12}De^{i\delta t}, \tag{5b}$$

$$\dot{c}_{21}=(1/2\hbar)V_{21}De^{-i\delta t}, \tag{5c}$$

where we have chosen the following conventions:

$$\omega_{12}=-\omega_{21}>0;\quad \delta=\omega_{12}-\omega. \tag{6}$$

SECTION II

Equations (5) can be solved rigorously. Differentiation of (5a) and substitution from (5b, c) gives:

$$\ddot{D}=-(1/\hbar^2)|V_{12}|^2D \\ -(i\delta/\hbar)[V_{12}c_{21}e^{i\delta t}-V_{21}c_{12}e^{-i\delta t}].$$

Again differentiating, substituting from (5b, c) and finally using (5a), we obtain

$$\dddot{D}=-\{(|V_{12}|/\hbar)^2+\delta^2\}\dot{D}.$$

The general integral of this equation is

$$D=\alpha\cos\Omega(t-T)+\beta, \tag{7}$$

where

$$\Omega^2=(|V_{12}|/\hbar)^2+\delta^2$$

and α, β, T are (real) constants. If the last collision occurred at $t=t_0$, our assumption that a collision restores the Boltzmann population requires the following boundary conditions on the density matrix

$$\left.\begin{aligned} c_{12}&=0=c_{21}\\ D&=D_0 \end{aligned}\right\}\text{ at } t=0, \tag{8}$$

where D_0 is the value appropriate to thermal equilibrium. The first two conditions imply by (5a) that $\dot{D}=0$ at $t-t_0$; this in turn implies that $T=t_0$ in (7).

Writing (7) in complex form, substituting in (5b), and integrating, we find:

$$c_{12}=\frac{V_{12}}{2\hbar}\left\{ie^{i\delta t}\left[\frac{\alpha e^{-i\Omega(t-t_0)}}{2(\Omega-\delta)}-\frac{\alpha e^{i\Omega(t-t_0)}}{2(\Omega+\delta)}-\frac{\beta}{\delta}\right]+\gamma\right\}, \tag{9}$$

where γ is an integration constant. Applying the first condition in (8),

$$\gamma=ie^{i\delta t_0}\{(\beta/\delta)-(\delta\alpha\hbar^2/|V_{12}|^2)\}.$$

A final relation on the integration constants is obtained as follows. Substitute (9) on the right of (5a) and (7) on the left. After some algebraic reduction, it will then be found that, if the resulting equation is to hold for all t, γ must be zero. This fact and the last of conditions (8) enable us to evaluate α and β. The final result is

$$D=(D_0/\hbar^2\Omega^2)\{|V_{12}|^2\cos\Omega(t-t_0)+(\hbar\delta)^2\}. \tag{10}$$

SECTION III

We are now in a position to show that the approximation used in obtaining (5) is a consistent one. More specifically, we shall show that (7) and (9) plus small rapidly varying terms form a good approximation to the solution of (4).

Make the *ansatz*:

$$D=D^{(0)}+d;\quad c_{12}=c_{12}^{(0)}+c, \tag{11}$$

where $D^{(0)}$ and $c_{12}^{(0)}$ are given by (7, 9) and where d and c are rapidly varying functions which are smaller than $D^{(0)}$ and $c_{12}^{(0)}$ by a factor of the order of the frequency of variation. Then $\dot{d}$ and $\dot{c}$ will be of the order of $D^{(0)}$ and $c_{12}^{(0)}$.

Substitute (11) into (4) and use the fact that $D^{(0)}$ and $c_{12}^{(0)}$ are rigorous solutions of (5). Neglecting terms of the order of d and c one obtains the following results, which show that d

and c do indeed have the properties assumed.

$$i\hbar\dot{d}=e^{i(\omega_{12}+\omega)t}V_{12}c_{21}^{(0)}+e^{-i(\omega_{12}+\omega)t}V_{21}c_{12}^{(0)},$$

$$i\hbar\dot{c}=c_{12}^{(0)}(V_{11}-V_{22})\sin\omega t-ie^{i(\omega_{12}+\omega)t}V_{12}D^{(0)}.$$

These could have been used to increase the accuracy of our solution (10).

SECTION IV

The change in the expectation value for the energy of the system since the last collision is given by

$$\Delta E=(\rho_{11}E_1+\rho_{22}E_2)\Big|_{t_0}^{t}.$$

Using (3) and the fact that the diagonal sum of ρ has the constant value unity, we may express ΔE in terms of D. When (10) is used, the final expression is found to be

$$\Delta E=(D_0\omega_{12}|V_{12}|^2/2\hbar\Omega^2)[1-\cos\Omega(t-t_0)].$$

Since the pressure has been assumed to be low, the probability that a given molecule will undergo collision during any short time interval will be proportional to the length of the interval and independent of the history of the molecule. It then follows that the probability that the last collision occurred during the interval $t-\theta$ to $t-\theta-d\theta$ is given by $e^{-\theta/\tau}d\theta/\tau$, where τ is the mean time between collisions. Setting $t_0=t-\theta$ above and integrating the product of these expressions from $\theta=0$ to $\theta=\infty$, we obtain the average change in the expectation value for the energy.

$$\langle\Delta E\rangle=\frac{D_0|V_{12}|^2\omega_{12}\tau^2/2\hbar}{1+\tau^2[\delta^2+(|V_{12}|/\hbar)^2]}. \tag{12}$$

When a collision next occurs, the expectation value of the energy will return to its Boltzmann value, while the excess will be carried off as thermal motion of the molecules. The mean rate of collisions per unit volume is N/τ where N is the number of molecules per unit volume in the two states considered. (Thus ND_0 is the thermal equilibrium value for ΔN, the population difference of the two levels.) The power absorbed per unit volume is therefore $N\langle\Delta E\rangle/\tau$.

For dipole radiation, V in (2) is equal[4] to the dot product of the dipole moment and the electric (or magnetic) field. Assuming an incident plane wave and allowing for the random spatial orientation of the molecule,

$$|V_{12}|^2=|\mu|^2 8\pi G/3c,$$

where μ is the dipole moment effective in the transition and G is the average incident power per unit area.

Making these substitutions and converting from angular to actual frequency, the power P absorbed by the gas per unit volume is given by

$$P=\frac{4\pi G\Delta N|\mu|^2\nu_0/3hc\tau}{(\Delta\nu)^2+(1/2\pi\tau)^2+(8\pi G|\mu|^2/3h^2c)}. \tag{13}$$

As mentioned earlier, if more than two levels are active but if no level can make a transition to more than one other level, then the absorptions of the several pairs as given by (13) can be added to give the total absorption.

Note that (13) reduces to the usual formula for low G and gives the correct limiting absorption $\Delta Nh\nu_0/2\tau$ for large G.

CONCLUSIONS

The formula (13) definitely predicts an additional broadening of the spectral line as G increases. The functional form checks the experimental results of Pond and Cannon[3] to well within experimental error. (It is easily shown from (13) that, in their notation, $\alpha_0(\Delta\nu)^2$ should be independent of incident power and proportional to the square of the pressure.) Since Pond and Cannon give their results in arbitrary units, a quantitative check cannot be made.

Because the term proportional to G in the denominator of (13) merely adds to the square of the usual line-breadth constant, the power level at which any given saturation effect on line shape occurs will be proportional to the square of the pressure as noted earlier by Townes.[1]

Accordingly, the theory presented here predicts broadening due to saturation and agrees with the experimental results available at this time.

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[4] P. I. Richards, Phys. Rev. **73**, 254 (1948).