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Inhaltsverzeichnis.

Line Width.

By

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With 19 Figures.

A. Early line broadening theory.

1. The bases for line broadening. It would seem that three avenues of approach to the problem of line width are open to us. First we might consider the historical aspects of the problem through a short study of the early attempts at description of the phenomena involved. Or we might instead begin with a qualitative description of the various conditions under which a line is broadened. Finally the early work of Michelson in organizing this field and developing certain phases of it was so successful that as a third alternative we are allowed the fortunate choice of a combination of the first two. Consequently our decision is not long in doubt.

Whether one considers the radiation-emitting atom as a classical oscillator or a quantum system possessed of discrete energy levels, one would at first be led to expect the emission of homogeneous radiation. Instead of this one finds the spectral line of definite width and shape, and it was toward a complete explanation of the causes of this phenomenon that Michelson [9] turned his attention in 1895.

Michelson began by summarizing the hypotheses which had previously been advanced as explanations of this phenomenon, namely,

1. Kirchhoff's law has as a consequence that two immediately contiguous portions of a bright line spectrum will have a decreasing ratio of brightness with an increasing path length in the absorbing or emitting gas.

2. Neighboring atoms will cause a direct modification of the period of the vibrating atoms.

3. The radiating away of energy by the oscillator will result in an exponential decrease in the vibrational amplitude.

4. The Doppler effect arising from the translational velocity component in the line of sight will result in a change in the wavelength of the emitted radiation.

To these causes of line broadening Michelson added the following:

5. Collisions with other atoms will cause a limitation of the number of regular vibrations by rapid changes of phase amplitude or plane of vibration.

6. Differences may exist in atomic properties which differences are so slight as to escape detection by other than spectroscopic means.

Now by a utilization of this rather historical compilation we may describe the various fashions in which a line is broadened.

We begin by removing our emitting atom to an infinite distance from all other atoms and reducing its effective temperature so that the atom is at rest. Under these conditions a spectral line emitted by this atom displays its "natural" shape. This natural line shape is due, in the classical sense, to precisely the effect given by MICHELSON as his third broadening agency. We shall discuss the phenomenon in a great deal more detail.

Next we raise the effective temperature of the atom, thus giving it some finite translational velocity. A given velocity component in the line of sight will result in a change in the frequency of the emitted radiation according to the well-known DOPPLER effect. A Maxwellian distribution of velocities will lead us to expect, for a given temperature, various velocities with various probabilities. As a consequence, the shifted frequencies corresponding to those velocities will be expected with varying probabilities, and a particular spectrum of frequencies of a certain width will then be anticipated for a given temperature.

These natural and DOPPLER effects may be expected to prevail in the absence of any neighboring atoms but, for the additional broadening effects present in any gaseous assembly, we must bring in these neighbors from infinity. Having done so, we look to MICHELSON's second and fifth effects to explain the additional line broadenings which will result. Indeed it is well we do so, for any other reasons for the broadening of spectral lines by neighboring atoms have yet to be advanced.

As we shall see in more detail, *the two general theories which dominate the line broadening field are the Statistical and Interruption theories.* It is true that these have been modified, correlated, joined, separated, limited, and smeared, but the statement remains approximately valid. Thus, it is interesting to note that the second of our listed factors forms the basis for the Statistical Theory and the fifth of these factors the basis for the Interruption Theory. That we have here the basis for the Interruption Theory should come as no great surprise since the father of this theory is, of course, MICHELSON.

In the Statistical Theory we shall see quantum energy levels distorted by interaction with atomic neighbors so that a shifting of the emitted frequencies and a broadening of the spectral line results. The classical analog of this phenomenon is MICHELSON's cause two.

We shall detail MICHELSON's first presentation of the Interruption Theory after a brief consideration of the DOPPLER effect. Let us first remark, however, that the sixth listed factor, although MICHELSON's shrewd prediction of isotopic spectra, is a form of pseudo-broadening—as is the first factor—which would be out of place in this treatment.

2. The DOPPLER effect in line broadening. The DOPPLER effect in line broadening was originally developed by RAYLEIGH [*10*] in 1889. EBERT[1] had considered the problem with all the molecules of the gas moving with the same velocity, but had ended by predicting lines of much greater width than those actually observed. This led RAYLEIGH to a consideration of the problem, as much in defense of the kinetic theory as in search of an explanation for line broadening. Instead of a constant velocity RAYLEIGH chose a Maxwellian distribution for the velocities. In this lay the difference.

Let us recall that a wavelength shift from λ to λ', where

$$\lambda' \approx \lambda\left(1 - \frac{\xi}{c}\right) \tag{2.1}$$

takes place in the radiation due to an emitter velocity component ξ in the line of sight.

Eq. (2.1) may be rewritten as

$$\xi^2 = \lambda^2 (\Delta \nu)^2 \tag{2.2}$$

[1] H. EBERT: Ann. Physik **36**, 466 (1889).

where $\Delta\nu$ is the frequency separation from the frequency of the emitted radiation for $\xi=0$.

Accordingly then, the distribution of frequencies in the spectral line will be given by the Maxwellian distribution:

$$I(\nu) = I_0 e^{-\frac{m}{2kT}\xi^2} = I_0 e^{-\frac{m\lambda^2(\nu-\nu_0)^2}{2kT}}, \tag{2.3}$$

where now I_0 is a constant equal to the intensity at line center where $\nu=\nu_0$.

Now let us define a quantity "half-width" as twice the frequency separation from line center of that frequency for which the intensity of the radiation has fallen to one half its maximum value. For the DOPPLER broadening then, an inspection of Eq. (2.3) tells us that the half-width, δ, is given by

$$\delta = \frac{2}{\lambda}\sqrt{2\frac{kT}{m}\log 2}. \tag{2.4}$$

3. The MICHELSON treatment of interruption broadening. We can return now to MICHELSON'S fifth broadening factor and the manner in which he introduced what we shall call the Interruption Theory of Broadening by his utilization of this factor.

We begin, with MICHELSON, by considering the emitting atom as moving among its neighbors and undergoing the collisions which would be expected when impenetrable spheres are taken as atomic models. We suppose these collisions to so change the phase that there is no coherence between the radiation emitted just prior and just subsequent to one of these collisions. For our purposes then we may consider the emission of a wave train terminated by a collision. The picture that then emerges of this interrupted emission phenomenon is as follows:

A collision has just been undergone by the emitter, and it now begins the emission of an electromagnetic wave of its natural frequency—in the case of our classical oscillator model, the frequency of its normal vibration. The atom continues to emit the wave train of the same frequency until it undergoes its next collision at which time this radiation is abruptly terminated. If the time between the collisions is taken as τ, then a wave train of frequency, say, ν_0, and length $c\tau$ has been emitted. We now perform a FOURIER analysis of this finite wave train to obtain our interruption broadened spectral line.

We shall not write down here the mathematics of MICHELSON'S derivation since this should more properly be consigned to the specific chapter on interruption broadening. We might remark briefly on the FOURIER transform for our present purposes.

Now the FOURIER transform has for its basis the fact that any function may be represented by the judicious choice of imaginary exponential functions, the method of rendering the choice judicious being the FOURIER transform. Each of these imaginary exponential functions, on the other hand, represents a wave train of infinite extension. Thus, in applying the FOURIER transform to a wave train of frequency ν_0 and finite extent we are simply building up the finite train from an infinite number of infinite trains, each of which differs very slightly in frequency from its nearest neighbor—frequencywise. Varying proportions, one might say, of the various infinite trains are needed in building up our finite train. For example, one might expect that the infinite train present in greatest proportion would be the train of frequency ν_0, the frequency of the cut-off wave train. The mixing proportions of the various trains are adjusted by adjusting the amplitudes of the waves involved. Thus, the intensity of a radiation frequency in the final, broadened spectral line will be proportional to the square of the requisite amplitude, that is, the square of the mixing proportion for the infinite wave train of that frequency.

After this fashion then, one is able to obtain a line of definite width by terminating emission at collision and performing a FOURIER transform of the cut-off emission. In this manner MICHELSON obtained

$$I(\nu) = a\,\frac{\sin^2[\pi\,\tau\,(\nu-\nu_0)]}{\pi^2\,(\nu-\nu_0)^2}\,. \tag{3.1}$$

MICHELSON used the value of τ obtainable from the mean free path and the mean atomic translational velocity. If we should now average Eq. (3.1) over a distribution of τ's, the resulting line shape would correspond to that obtained some ten years later by LORENTZ.

4. The LORENTZ theory. The LORENTZ derivation [5] of a spectral line shape is of contemporary interest primarily from a historical viewpoint, although it does provide the unique example of the obtention of a line shape by a classical study of the mechanics of absorption of radiation by a vibrating electron. Essentially we do the following.

First an expression is obtained for x, the vibrational coordinate of an atomic photoelectron, in the presence of an external electromagnetic field. As we may recall, the vibrations of the bound photoelectron of an atom provide the mechanism for the emission and absorption of electromagnetic radiation by an atom in the classical picture. Now in the resulting equation for x certain boundary conditions are necessary for the evaluation of two constants which appear. It is through these boundary conditions that the effects of collision first enter. Again the termination of radiation by collisions is assumed. Further, it is supposed that, immediately subsequent to the last collision undergone by the molecule under consideration, a random distribution such that

$$x = \dot{x} = 0 \tag{4.1}$$

existed, and the boundary conditions are thus furnished. Next, x is averaged over a distribution of inter-collision times, τ. We are thus able to show that collisions have the same effect on x as does the introduction of a damping force into the original equation for x. Then the relevant MAXWELL equations are solved to yield the absorption coefficient for the spectral line. Let us detail this calculation.

First we shall show the equivalence between an atomic collision (in the MICHELSON-LORENTZ sense) and a damping force.

The behavior of an electron acted on by a linear restoring force $-fx$, a damping force $-g\dot{x}$, and an external electric field $E_x = a e^{i\omega t}$ may be described classically by the equation:

$$m\ddot{x} = -fx - g\dot{x} + e a\,\mathrm{e}^{i\omega t} \tag{4.2}$$

wherein e is the electronic charge.

Eq. (4.2) has the solution

$$x = \frac{a e}{m\,(\omega_0-\omega)^2 + i\,\omega\,g}\,\mathrm{e}^{i\omega t} \tag{4.3}$$

where $\omega_0^2 = f/m$ is the natural vibrational frequency of the electron.

On the other hand, the removal of the damping force $-g\dot{x}$ results in an electronic equation

$$m\ddot{x} = -fx + e a\,\mathrm{e}^{i\omega t} \tag{4.4}$$

of solution

$$x = \frac{a\,e}{m\,(\omega_0^2 - \omega^2)}\,e^{i\omega t} + C_1\,e^{i\omega_0 t} + C_2\,e^{-i\omega_0 t}. \tag{4.5}$$

It is for the evaluation of C_1 and C_2 that we must needs introduce boundary conditions.

Now let us suppose that the last collision was experienced by our emitter just before time $t-\vartheta$. Then at time $t-\vartheta$ we suppose there to have been a random distribution of the x and $\dot{x}$ such that Eq. (4.1) held at the time. This condition furnishes the equations for the evaluation of C_1 and C_2 with the result

$$x = \frac{a\,e}{m\,(\omega_0^2 - \omega^2)}\,e^{i\omega t}\left\{1 - \frac{1}{2}\left(1 + \frac{\omega}{\omega_0}\right)e^{i(\omega_0-\omega)\vartheta} - \frac{1}{2}\left(1 - \frac{\omega}{\omega_0}\right)e^{-i(\omega_0+\omega)\vartheta}\right\}. \tag{4.6}$$

The probability of a time ϑ having elapsed since the last collision is $\frac{1}{\tau}\,e^{-\vartheta/\tau}$ where τ is the average time between collisions. When Eq. (4.6) is averaged over this distribution, there results:

$$\langle x\rangle = \frac{a\,e}{m\left(\omega_0^2 + \frac{1}{\tau^2} - \omega^2\right) + 2\,\frac{i\,m\,\omega}{\tau}}\,e^{i\omega t}. \tag{4.7}$$

A comparison of Eqs. (4.3) and (4.6) suffices to tell us that the atomic collisions have the same effect on the electronic motion as a damping constant $g = 2m/\tau$ and linear restoring force constant $f_c = f + \frac{m}{\tau^2}$. Let us again consider Eq. (4.2).

A polarizable medium of polarizability α adds the term $e\alpha P_x$ to Eq. (4.2). Further:

$$P_x = N\,e\,x \Leftrightarrow \dot{P}_x = N\,e\,\dot{x}$$

so that we may now rewrite this equation as

$$\frac{m}{N\,e^2}\,\ddot{P}_x = E_x + \alpha\,P_x - \frac{f}{N\,e^2}\,P_x - \frac{g}{N\,e^2}\,\dot{P}_x. \tag{4.8}$$

The assumptions

$$E_x = E_{0x}\,e^{i\omega t};\qquad P_x = P_{0x}\,e^{i\omega t}$$

lead to

$$E_{0x} = (\xi + i\eta)\,P_{0x} \tag{4.9a}$$

where

$$\xi = \frac{f}{N\,e^2} - \alpha - \frac{m\,\omega^2}{N\,e^2};\qquad \eta = \frac{\omega\,g}{N\,e^2}. \tag{4.9b}$$

A complete description of the radiation field must, of course, include the magnetic field and the propagation. We take the propagation direction as the z-direction so that the exponential factor in the field vectors is now $\exp[i\omega\,(t - q\,z)]$ and suppose that $\boldsymbol{E} = \boldsymbol{i}\,E_x$ and $\boldsymbol{H} = \boldsymbol{j}\,H_y$. MAXWELL's equations then lead to the relations

$$q\,H_y = \frac{1}{c}\,D_x;\qquad q\,E_x = \frac{1}{c}\,H_y \tag{4.10}$$

which means that

$$D_x = c^2 q^2 E_x \Leftrightarrow P_x = (c^2 q^2 - 1)\,E_x. \tag{4.11}$$

A comparison of Eqs. (4.9a) and (4.11) shows

$$c^2 q^2 - 1 = \frac{1}{\xi + i\eta}. \tag{4.12}$$

Now surely one may write

$$q = \frac{1 - i\chi}{\Upsilon} \Leftrightarrow e^{i\omega\left(t - z\frac{1 - i\chi}{\Upsilon}\right)} \tag{4.13}$$

which means that the field vectors are attenuated by the factor

$$e^{-\frac{\omega\chi}{\Upsilon}z}. \tag{4.14}$$

We substitute Eq. (4.13) into Eq. (4.12) with the result

$$\frac{2c^2}{\Upsilon^2} = \sqrt{\frac{(\xi+1)^2+\eta^2}{\xi^2+\eta^2}} + \frac{\xi}{\xi^2+\eta^2} + 1 \tag{4.15a}$$

$$2\frac{c^2\chi^2}{\Upsilon^2} = \sqrt{\frac{(\xi+1)^2+\eta^2}{\xi^2+\eta^2}} - \frac{\xi}{\xi^2+\eta^2} - 1. \tag{4.15b}$$

The radical in Eq. (4.15b) is expanded according to the binomial theorem and all terms after the third dropped as small with the result

$$2\frac{c^2\chi^2}{\Upsilon^2} = \frac{4\eta^2 - 4\xi - 1}{8(\xi^2+\eta^2)^2}. \tag{4.16}$$

All terms save the η^2 in the denominator of this equation may be dropped since $\eta^2 \gg \xi$ for $\eta \gg \xi$, and when $\xi \sim \eta$, the entire equation is small. The absorption coefficient may then be obtained as

$$\mathfrak{k} = \frac{\omega\chi}{\Upsilon} = \frac{\omega}{c}\left(\frac{c\chi}{\Upsilon}\right) = \frac{\omega}{2c}\,\frac{\eta}{\xi^2+\eta^2} = \frac{N m e^2}{c\tau}\,\frac{\nu^2}{(\nu_0-\nu)^2 + \frac{4m^2}{\tau^2}\nu^2} \tag{4.17}$$

which may be displayed in a more familiar form.

Firstly the half-width of this distribution is given by

$$\delta = \frac{4m}{\tau}\nu \tag{4.18}$$

and the integrated absorption by

$$S = \int_{-\infty}^{+\infty} \mathfrak{k}\, d\nu_0 = \frac{2\pi}{\delta}\,\frac{N m e^2}{c\tau}\,\nu^2 \tag{4.19}$$

so that Eq. (4.16) may be rewritten as

$$\mathfrak{k}(\nu_0) = \frac{S}{\pi}\,\frac{(\delta/2)}{(\nu_0-\nu)^2 + (\delta/2)^2} \tag{4.20}$$

which is the more familiar form of the LORENTZ line shape equation.

Actually Eq. (4.20) attenuates the field vectors, and we are interested in the attenuation of the energy. If we reinterpret S as the integrated absorption coefficient for the energy when $\varkappa = 2\mathfrak{k}$, then we obtain Eq. (4.20) for $\varkappa$, the absorption coefficient for the energy.

B. Interruption broadening

5. Early quantum justifications of the FOURIER transform. After the advent of the quantum theory it was not generally felt that the MICHELSON-LORENTZ Interruption Theory could be accepted without some further justification in the light of the transition from the classical to the quantum physics. The first attempts at justification proceeded from the classical to the quantum while later attempts—twenty and more years later—were just the other way round. One does sometimes receive the impression that the approximating ability of some of the authors is perhaps overtaxed.

The first quantum justification of the use of the classical FOURIER transformation in the manner of MICHELSON was a simple appeal to correspondences by LENZ[1] which was perhaps as good a justification as any, if rather qualitative. In this appeal, two broadening agencies are assumed.

In the first of these, collisions are supposed to completely transform excitation energy into translational energy. In the quantum case a certain percentage of the atoms in a gas radiate while the remainder lose their excitation energy by collision. This corresponds to the classical case wherein the emitting oscillator radiates a portion of its energy and loses the remainder on collision.

In the second type of collision a so-called optical collision occurs during the passage of a perturber at some minimum distance. At this minimum an instantaneous large perturbation of the emitted radiation frequency is presumed. Then between two such collisions defined radiation is emitted which may be analyzed according to FOURIER.

Now WEISSKOPF [*11*] presented a quantum justification of the FOURIER transform of a much quantitative nature to which JABLONSKI has taken some exceptions which we shall mention. WEISSKOPF set the SCHRÖDINGER equation for the problem up in one dimension which JABLONSKI[2] felt was a rather poor way to treat a central force problem. This latter author was of the opinion that this merely camouflaged the difficulty at the turning point of the classical motion rather than easing it. JABLONSKI also objected to WEISSKOPF'S apparent failure to properly quantize the translational motion. These criticisms appear important primarily in emphasizing that the interruption picture of line broadening is only a limiting approximation to the solution of the actual broadening problem, a point which easily may be overlooked.

Whether approximate or otherwise, however, these justifications do provide a basis for the later investigations of the Interruption Theory.

6. The interruption shape with zero collision time. Let us consider the oscillating dipole moment—the oscillating photoelectron—of the emitter. We suppose it to be given by

$$M(t) = \text{const} \cdot \exp\left[i \int_0^t \omega_0(t')\, dt'\right]$$

and the FOURIER amplitude by

$$J(\omega) = \int_{-\infty}^{+\infty} M(t)\, e^{-i\omega t}\, dt = \text{const} \int_{-\infty}^{+\infty} \exp\left[i\left\{\int_0^t \omega_0(t')\, dt' - \omega t\right\}\right] dt. \tag{6.1}$$

We suppose $\omega_0(t)$ to be a constant between two "optical collisions"—which are yet to be defined—and completely undefined during these collisions. As in

[1] W. LENZ: Z. Physik **25**, 299 (1924).
[2] A. JABLONSKI: Phys. Rev. **68**, 78 (1945).

Sect. 3, we simply perform a FOURIER analysis of the cut off wave train thus emitted during time τ, the intercollision time

$$J(\nu) = \text{const} \int_{-\tau/2}^{\tau/2} e^{2\pi i(\nu_0-\nu)t}\, dt = \text{const} \frac{\sin[\pi(\nu_0-\nu)\tau]}{\pi(\nu_0-\nu)} \tag{6.2a}$$

so that:

$$I'(\nu) = |J(\nu)|^2 = \text{const} \frac{\sin^2[\pi(\nu_0-\nu)\tau]}{\pi^2(\nu_0-\nu)^2} \tag{6.2b}$$

which, of course, corresponds precisely to Eq. (3.1). As did LORENTZ in obtaining Eq. (4.7), we now average Eq. (6.2b) over all τ as follows:

$$I(\nu) = \int_0^\infty I'(\nu)\, e^{-\tau'/\tau}\, d\tau' = \text{const} \frac{(1/2\pi\tau)}{(\nu_0-\nu)^2 + (1/2\pi\tau)^2} \tag{6.3}$$

where, of course,

$$\delta = \frac{1}{\pi\tau} = \frac{1}{\pi}\frac{\langle v\rangle}{l} = \langle v\rangle N \varrho^2 \tag{6.4}$$[1]

with $\langle v\rangle$ the relative velocity. If we were to assume MICHELSON's hard spheres as the atomic models, a collision would take place when the center of the emitter were separated by an atomic diameter from the center of a broadener. The diameter would then be the ϱ of Eq. (6.4). In the WEISSKOPF version of the Interruption Theory, however, ϱ is the "optical collision diameter" which we now define.

Let us consider Eq. (6.1), in particular $\int_0^t \omega_0(t')\, dt'$. In this expression $\omega_0(t')$ is the vibrational frequency of our photoelectron. Further we suppose $\omega_0(t')$ to change with time as a result of an interaction between emitter and broadener. Let us write

$$\int_0^t \omega_0(t')\, dt' = \omega_0 t + \int_0^t \Delta(r)\, dt' = \omega_0 t + \eta \tag{6.5}$$

wherein we have supposed that the frequency perturbation is a function of emitter-broadener separation r. Now we assume that when η has attained some specific value, an optical collision has taken place, and the emitted wave train is cut off and FOURIER analyzed.

Some value of η has to be assumed as defining a collision, and WEISSKOPF felt that $\eta = 1$ was a reasonable value. This assumption, although admittedly rather arbitrary, allows the evaluation of the optical collision diameter ϱ. Let us consider a VAN DER WAALS interaction ($\Delta(r) = C/r^6$) between emitter and broadener, thus precluding self-broadening at least. Further, the phase change is presumed to occur during the collision of duration t so that the extension of the limits of integration in Eq. (6.5) will not affect the value of η. Letting $x = vt/\varrho$,

$$\eta = \int_{-\infty}^{+\infty} \frac{C\, dt}{(\langle v\rangle^2 t^2 + \varrho^2)^3} = \frac{C}{\varrho^5 \langle v\rangle} \int_{-\infty}^{+\infty} \frac{dx}{(x^2+1)^3} = \frac{C}{\varrho^5\langle v\rangle}\left(\frac{3\pi}{8}\right) \tag{6.6a}$$

[1] Some authors have used root mean square relative velocity while others have used mean relative velocity.

which is ~1 by our assumption so that

$$\varrho = \left(\frac{3\pi C}{8\langle v\rangle}\right)^{\frac{1}{5}} \tag{6.6b}$$

for the VAN DER WAALS interaction where C is in angular frequency units, ω.

This then is the LENZ-WEISSKOPF modification of the early MICHELSON-LORENTZ Interruption Theory. For certain applications it remains quite useful. Let us consider Fig. 1 in an attempt to provide a clearer physical picture of the implications of this theory.

To begin with we suppose the arrow to represent the emitter path while the circles represent perturbers. Specifically the circles marked A are perturbers which are too distant from the emitter path to cause a phase shift of one while the perturbers B are sufficiently close to induce such a shift. At point b on the perturber path the separation of the B broadener and the emitter is such that an optical collision has just terminated. Thus, our emitter will begin to emit again as it proceeds along its path from point b. It will pass among the A perturbers, but, al though they will affect the emitter, no collision in the WEISSKOPF sense will take place until the point c is reached. At this point $\eta=1$ so that a collision has taken place. Radiation is terminated, and the emission between points b and c is FOURIER analyzed. Specifically then, we have neglected two possible contributions to line shape, (1) the effect of the distant collisions with the A perturbers and (2) the effect of the near collisions resulting in phase shifts of $\eta>1$, as for example would take place along the paths $a\to b$ and $c\to d$. This neglect of close collisions might also be considered as a failure to include the "time of collisions".

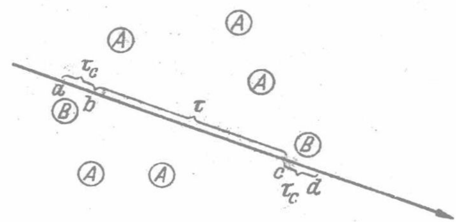

Fig. 1. A model of the physical conception inherent in the WEISSKOPF Interruption Theory.

These are the discrepancies which seem to appear in the physical picture and they might perhaps be associated with certain discrepancies which show up in our line shape. Supposedly Eq. (6.3) gives the line shape regardless of the interatomic interactions responsible for the shape with Eq. (6.6b) furnishing the optical collision diameter for the VAN DER WAALS interaction. Since experimental evidence would lead us to expect a line shift and a line asymmetry in this case, the result is rather disappointing. LENZ[1] first attempted to resolve this disparity by including the time of collision (which would correct our second neglect in the physical picture) but without too much success. LINDHOLM[2] later included (1) the effect of distant collisions quite successfully and this we shall consider. The author subsequently included (2) the effect of near collisions on the time of collision. We remark that (2) is no longer actually an interruption consideration and leads to a more general formulation. For this formulation we shall turn to the work of ANDERSON.

7. The distant collision included. If, in Eq. (6.1), we substitute Eq. (6.5), the amplitude may be written as

$$J(\nu) = \int_{-\infty}^{+\infty} e^{2\pi i(\nu-\nu_0)t + i\Delta(t)}\, dt$$

[1] W. LENZ: Z. Physik **80**, 423 (1933).

[2] E. LINDHOLM: Ark. Mat. Astron. Fys. A **28**, No. 3 (1942).

wherein, of course, $\eta = \Delta(t)$. This leads us to the following expression for the intensity:

$$\left.\begin{aligned} I(\nu) &= \Big|\int_{-\infty}^{+\infty} e^{2\pi i(\nu-\nu_0)t+i\Delta(t)}\,dt\Big|^2 \\ &= \iint_{-\infty}^{+\infty} e^{2\pi i(\nu-\nu_0)(t''-t')+i[\Delta(t'')-\Delta(t')]}\,dt'\,dt'' \\ &= \int_0^{+\infty} e^{2\pi i(\nu-\nu_0)t}\,dt \int_{-\infty}^{+\infty} e^{i[\Delta(t+t')-\Delta(t')]}\,dt' \end{aligned}\right\} \tag{7.1}$$

and we have let $t = t'' - t'$.

We now introduce a concept—originally due to LENZ[1]—which has been extensively used in evaluating the second of the two integrals in Eq. (7.1), the integral which was later to be dubbed "correlation function". If we assume a random distribution in time, then this second integral may be considered the statistical time mean of $\exp\{i[\Delta(t+t')-\Delta(t')]\}$. We may recall the use of the ergodic hypothesis to infer the fact that the statistical time mean is equivalent to the statistical mean. A method of evaluation of this integral is then to determine the statistical mean of this exponential.

Next it is assumed that three different phase changes may occur on collision. The number three is completely arbitrary and could be increased to any desired number. The mean time between collisions is τ, and the phase changes are η_a, η_b, and η_c. The probability of n collisions of phase change η_a, m collisions of phase change η_b, and l collisions of phase change η_c is

$$\frac{(n+m+l)!}{n!\,m!\,l!}\left(\frac{\sigma_a}{\sigma}\right)^n\left(\frac{\sigma_b}{\sigma}\right)^m\left(\frac{\sigma_c}{\sigma}\right)^l \tag{7.2a}$$

where $\sigma = \sigma_a + \sigma_b + \sigma_c$ is the collision cross-section. The probability of the $n+m+l$ collisions occurring during time t is

$$\frac{1}{(n+m+l)!}\left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau} \tag{7.2b}$$

so that the probability for occurrence of n a-collisions, m b-collisions, and l c-collisions of mean intercollision time τ during the time t is

$$\left(\frac{\sigma_a}{\sigma}\right)^n\left(\frac{\sigma_b}{\sigma}\right)^m\left(\frac{\sigma_c}{\sigma}\right)^l \frac{1}{n!\,m!\,l!}\left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau}. \tag{7.3}$$

Now by our definitions,

$$\Delta(t+t') - \Delta(t') = n\,\eta_a + m\,\eta_b + l\,\eta_c.$$

We may now return to the evaluation of the second integral in Eq. (7.1) which may be written as

$$\left.\begin{aligned} &\langle e^{i[\Delta(t+t')-\Delta(t')]}\rangle \\ &= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{l=0}^{\infty}\left(\frac{\sigma_a}{\sigma}\right)^n\left(\frac{\sigma_b}{\sigma}\right)^m\left(\frac{\sigma_c}{\sigma}\right)^l\frac{1}{n!\,m!\,l!}\left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau}\left\{e^{i[n\eta_a+m\eta_b+l\eta_c]}\right\}. \end{aligned}\right\} \tag{7.4}$$

Further:

$$\sum_{n=0}^{\infty}\left(\frac{\sigma_a\,t\,e^{i\eta_a}}{\sigma\tau}\right)\frac{1}{n!} = \exp\left[\frac{\sigma_a t}{\sigma\tau}\,e^{i\eta_a}\right]$$

[1] l. c., footnote 1 on p. 9.

so that Eq. (7.4) becomes

$$\langle e^{i[\Delta(t+t')-\Delta(t')]}\rangle = e^{\frac{t}{\tau\sigma}[\sigma_a e^{i\eta_a}+\sigma_b e^{i\eta_b}+\sigma_c e^{i\eta_c}]\, e^{-t/\tau}}. \tag{7.5}$$

Eqs. (7.1) and (7.5) lead to

$$I(\nu) = \int e^{-\frac{t}{\tau\sigma}\sum_i[\sigma-\sigma_i\cos\eta_i]} \cos\left[\frac{t}{\tau\sigma}\sum_i \sigma_i\sin\eta_i + 2\pi(\nu-\nu_0)\,t\right] dt. \tag{7.6}$$

We now let

$$t\sum_i \frac{\sigma_i}{\sigma\tau}[\sigma-\sigma_i\cos\eta_i] = \alpha\, t, \tag{7.7a}$$

$$t\sum_i \frac{\sigma_i}{\sigma\tau}\sin\eta_i = \beta\, t \tag{7.7b}$$

with the result

$$\left.\begin{aligned} I(\nu) &= \int_0^\infty e^{-\alpha t}\cos\{[2\pi(\nu-\nu_0)+\beta]\,t\}\,dt \\ &= \frac{\text{const}}{\left[(\nu-\nu_0)+\frac{\beta}{2\pi}\right]^2+\left[\frac{\alpha}{2\pi}\right]^2}. \end{aligned}\right\} \tag{7.7c}$$

The line shift is obviously given by β while the line width is just as obviously given by 2α. The problem of evaluation is the relatively straightforward one of phase shift evaluation in Eqs. (7.7). With a classical path assumption one may evaluate by equations of the form Eq. (6.6a) for example.

If we designate the broadening interactions as C/r^n then Eqs. (7.7) may be evaluated for several cases of interest:

n	δ_n	Δ_n
3	$4\pi^3 C N$	—
4	$3.88\, C^{\frac{2}{3}} v^{\frac{1}{3}} N$	$33.4\, C^{\frac{2}{3}} v^{\frac{1}{3}} N$
6	$17.0\, C^{\frac{2}{5}} v^{\frac{3}{5}} N$	$6.16\, C^{\frac{2}{5}} v^{\frac{3}{5}} N$

and in all cases the constant, the half-width, and the shift are in angular frequency units.

8. Detailed balancing. Let us diverge from the main stream of the development for a rather important subsidiary consideration.

Now the method, which VAN VLECK and MARGENAU[1] used to obtain the power absorbed per frequency interval in a form which agreed with the power emitted, was to obtain the work done by the radiation field on the oscillator *between* collisions and to this add the impulsive work done *at* collisions.

The power emitted by the oscillator may be obtained as

$$P_E(\omega) = \frac{(1/\tau)\,t'}{t'}[P_{E'}(\omega)] = \left[\frac{2}{3}\frac{e^2}{c^3}2\omega^4|x(\omega)|^2\right](1/\tau) \tag{8.1a}$$

where we have supposed

$$\ddot{x} = -\omega^2 x^2$$

and, since the FOURIER analysis of $x(\omega)$ is only carried out over the period between two collisions, in which we have averaged over a long period t'. One thus obtains

$$P_E(\omega) = \frac{e^2 x_0^2}{3\pi c^3}\omega^4\left[\frac{(1/\tau)}{(\omega_0-\omega)^2+(1/\tau)^2}+\frac{(1/\tau)}{(\omega_0+\omega)^2+(1/\tau)^2}\right]. \tag{8.1b}$$

[1] J. H. VAN VLECK and H. MARGENAU: Phys. Rev. 76, 1211 (1949).

We suppose collisions to occur at $t = t_1, t_2, \ldots$ and the equation to be satisfied is

$$\ddot{x} + \omega_0^2 x = \frac{e E_x}{m} \cos(\omega t + \varphi)$$

where

$$\begin{aligned} x &= x_1 \quad \text{for} \quad t_1 \le t \le t_2 \\ &= x_2 \quad \text{for} \quad t_2 \le t \le t_3, \text{ etc.} \end{aligned}$$

under the LORENTZ boundary conditions $\dot{x}_j(t_j) = x_j(t_j) = 0$. A solution is

$$x_j = \frac{e E_x}{m \omega} \int_0^{t-t_j} \cos(\omega t - \omega t' + \varphi) \sin(\omega_0 t')\, dt', \tag{8.2a}$$

$$\dot{x}_j = \frac{e E_x}{m c} \int_0^{t-t_j} \cos(\omega t - \omega t' + \varphi) \cos(\omega_0 t')\, dt'. \tag{8.2b}$$

Thus, the work done by the field on the oscillator between collisions is

$$\left.\begin{aligned} W &= \sum_j \int_{t_j}^{t_{j+1}} e E_x \cos(\omega t + \varphi)\, \dot{x}_j\, dt \\ &= \frac{e^2 E_x^2}{m} \sum_j \int_0^{\vartheta_j} \cos(\omega t + \varphi_i)\, dt \int_0^t \cos[\omega(t - t' + \varphi_j)] \cos \omega_0 t'\, dt' \end{aligned}\right\} \tag{8.3}$$

where

$$\vartheta_j = t_{j+1} - t_j \quad \text{and} \quad \varphi_j = \omega t_j + \varphi.$$

The distribution $\left(\frac{1}{\tau}\right)^2 t''\, e^{-\vartheta/\tau}$ is again applied to the intercollision times, the summation in Eq. (8.3) now being replaced by an averaging over this distribution. The time of observation is t''. A subsequent reduction of the trigonometric relations leads to

$$\left.\begin{aligned} \frac{W}{t''} &= \frac{1}{t''} \left[\frac{e^2 E_x^2}{2m} \left(\frac{1}{\tau}\right)^2 t'' \int_0^\infty e^{-\vartheta/\tau}\, d\vartheta \int_0^\vartheta dt \int_0^t \cos \omega t' \cos \omega_0 t'\, dt' \right] \\ &= \frac{e^2 E_x^2}{4m} \left[\frac{(1/\tau)}{(\omega - \omega_0)^2 + (1/\tau)^2} + \frac{(1/\tau)}{(\omega + \omega_0)^2 + (1/\tau)^2} \right] \end{aligned}\right\} \tag{8.4}$$

which is the work done per unit time (power) by the field on the oscillator between collisions. We now find the work done at collisions.

If t_{j+1} is the time of collision, then the boundary condition requires that $x_j(t_{j+1})$ be zero. In all probability $x_j(t_{j+1})$ will have some value not zero immediately prior to collision so that an instantaneously infinite velocity would be required to have $x_j(t_{j+1})$ zero. This has been objected to as not physically plausible, but when one admits it as a mathematical approximation—which is probably as reasonable as the collision model itself—it should not be too hard to accept. For the impulsive work at collision then

$$W_c = \lim_{t' \to 0} \int_{t_{j+1}-t'}^{t_{j+1}+t'} e E_x \cos(\omega t + \varphi)\, \dot{x}_j\, dt = -\sum_j e E_x \cos(\omega t + \varphi)\, x_j(t_{j+1}) \tag{8.5}$$