Asymmetries of Pressure Broadened Spectral Lines

HENRY MARGENAU, *Sloane Physics Laboratory, Yale University*
(Received August 28, 1933)

Experiments have disclosed peculiar asymmetries in the intensity distribution of pressure broadened lines. The present paper is devoted to their explanation. The simple case of a one-dimensional gas is considered and an expression for the line contour developed. By graphical methods we have calculated the line contours corresponding to three typical interaction curves. Results are given in Figs. 1 to 3. The conclusion is that, by taking proper account of the repulsive portions of the energy curves, the empirically found asymmetries can be reproduced.

THE effects of foreign gas pressure on an absorption line are usually a shift to the red and an asymmetrical broadening to the red. Both can be explained by assuming attractive forces, i.e., energy curves which increase with distance, between the absorbing atom in its higher state and the perturbers. There are, however, some noteworthy exceptions from this general rule. Füchtbauer and his collaborators[1] have observed that H_2 produces a red shift, but slight broadening to the blue in the line Hg 2537. The same effect exists for the *D*-lines of sodium[2] if H_2 is used as the perturbing gas.

Another rather interesting observation has recently been made by Füchtbauer and Gössler.[3] They find that different spectral lines of the same series (first three members of the principal series of Cs) show markedly different asymmetries if broadened by the same gas. Watson and Margenau[4] investigated the corresponding lines of potassium and found, though not an actual reversal of the asymmetry in passing from the second to the third member, as did Füchtbauer and Gössler, an indication of greater symmetry.

We know, of course, that these peculiar phenomena reflect some properties of the interaction curves, and it seems pertinent to inquire what they are. A tentative explanation of the first mentioned features has already been suggested;[2] it will be made more evident in this note. At the same time, the considerations here presented will illuminate the later findings of Füchtbauer and Gössler, Watson and Margenau. We shall make the simplest possible assumptions and study the effect of various shapes of interaction curves upon the intensity distribution within a pressure broadened line.

The method of calculation will be that used in a previous paper.[5] It consists in determining the probability of emission of a given frequency ν, and this probability is taken to be proportional to the relative time during which the system (absorbing atom + perturbers) is capable of absorbing this frequency, i.e., the time during which the vertical difference between the interaction curves for the upper and lower state has the value $h\nu$. This method of statistical analysis for the purpose of calculating line widths has been criticized by Lenz,[5] who claims that it leads to correct results only for extremely high pressures, and wishes to replace it by a Fourier analysis of the varying electric moment of the vibrating atom. It may be shown,[6] however, that the two methods lead to similar physical results, for they produce equal shifts, equal "standard deviations" of frequencies within the spectral line, and equal asymmetries. They differ only with regard to physically insignificant details. The method here chosen is applicable without pressure restrictions, although, to be sure, it neglects natural line width, Doppler effect, and collisions of the second kind, in which we are not at present interested.

[1] C. Füchtbauer, G. Joos and O. Dinckelacker, Ann. d. Physik **71**, 204 (1923).

[2] H. Margenau and W. W. Watson, Phys. Rev. **44**, 92 (1933).

[3] C. Füchtbauer and F. Gössler, Naturwiss. **21**, 315 (1933).

[4] W. W. Watson and H. Margenau, Phys. Rev. **44**, 748 (1933).

[5] W. Lenz, Zeits. f. Physik **80**, 423 (1933).

[6] Details will be given elsewhere.

To avoid lengthy calculations which, if carried through, introduce nothing essentially different from the simpler analysis here presented, we consider a one-dimensional case. The absorbing atom, regarded fixed at the origin, is subject to energy perturbations due to numerous perturbers, all of which move without appreciable accelerations along the x-axis. The latter will be considered distributed completely at random with regard to positions; we are neglecting the portion of the Boltzmann factor involving coordinates. The interaction between the absorbing atom and one perturber is described by two energy curves, one for the upper, and one for the lower state of the absorption. Let the energy difference between them minus the normal energy of the transition, for a given distance x from the origin, be $f(x)$. In general, the lower curve is nearly straight, so that $f(x)$ may be regarded as approximately the energy of the upper curve. If there are altogether n perturbers and the range to which they are confined is L, the intensity of frequency ν differing from the normal frequency ν_0 by $h\nu$ is found by integrating $dx_1dx_2\cdots dx_n/L^n$ over that part of configuration space in which $f(x_1)+f(x_2)+\cdots f(x_n)=V$. Hence, with the familiar Dirichlet factor,

$$I(V)dV=(L^{-n}/\pi)\int_{-\infty}^{\infty}d\rho[\sin(\tfrac{1}{2}\rho dV)/\rho]e^{-iV\rho}\int_0^L\cdots(n)\int_0^L e^{i\rho[f(x_1)+\cdots f(x_n)]}dx_1\cdots dx_n. \qquad (1)$$

The n-fold integral over configuration space is, of course, simply $[\int_0^L e^{i\rho f(x)}dx]^n$. We wish to evaluate (1), assuming for $f(x)$ a curve sufficiently general to permit comparison with physically plausible types of interaction. It is difficult to find an analytical expression for $f(x)$ that can be handled; hence it will be necessary to construct this function by compounding several straight lines. Difficulties in connection with infinite derivatives will not arise. Let $f(x)=\varphi(x)-v/L$, where $\varphi(x)$ is given by Fig. 2a, but with a not necessarily equal to d. We are subtracting the small quantity v/L to take account of the fact that $f(x)$ in reality approaches 0 only asymptotically, not at a finite distance x_3. Division of the constant v by L is an expedient way of insuring that the intensity distribution will not depend on the "volume" of the gas, in our case on the range L, but only on the pressure. An inspection of Eq. (1) shows at once that the effect of the term v/L in $I(V)$ is to replace every $f(x)$ by $\varphi(x)$ and V by $V+(n/L)v$. This merely means a constant displacement of the intensity curve along the abscissae, that is, a shift to the red. We can, therefore, by this simple artifice produce any red shift we desire and still account for the asymmetry of the line by a suitable choice of φ.

Denoting by α, β, γ the slopes of $\varphi(x)$ in the ranges: $(0,x_1)$, (x_1, x_2), (x_2, x_3), respectively, we have

$$\alpha=-a/x_1;\qquad \beta=-d/(x_2-x_1);\qquad \gamma=d/(x_3-x_2). \qquad (2)$$

Then, by dividing the range from 0 to L into four parts and adding the contributions of each, one finds after some simple algebra

$$\int_0^L e^{i\rho\varphi(x)}dx\equiv F(\rho)=(1/i\rho)[\alpha^{-1}(1-e^{i\rho a})+(\gamma^{-1}-\beta^{-1})(1-e^{-i\rho d})]+L-x_3.$$

If we substitute (2), write the exponentials as trigonometric functions and put $x/L=l$, this becomes

$$F(\rho)=L\left\{1-l_3+\frac{l_1}{\rho a}\sin\rho a+\frac{l_3-l_2}{\rho d}\sin\rho d+i\left[\frac{l_1}{\rho a}(1-\cos\rho a)-\frac{l_3-l_1}{\rho d}(1-\cos\rho d)\right]\right\}. \qquad (3)$$

Call the contents of the { }, diminished by 1, u. n being very large, it is permissible to replace $[F(\rho)]^n$ by L^ne^{nu}. This expression is to be introduced in (1) in place of the integral over configuration space. Before making the substitution, however, we observe that (1) can be written:

$$I(V)dV=\frac{L^{-n}}{\pi}\int_0^{\infty}d\rho\frac{\sin(\tfrac{1}{2}\rho dV)}{\rho}\{e^{-i(V+v')\rho}F(\rho)^n+e^{i(V+v')\rho}F(-\rho)^n\},$$

where v' is put for $(n/L)v$. Therefore, on account of (3),

$$I(V)dV=\frac{2e^{-nl_3}}{\pi}\int_0^\infty \frac{\sin\left(\frac{1}{2}\rho dV\right)}{\rho} e^{nl_1/\rho a\,\sin\,\rho a+n(l_3-l_1)/\rho d\,\sin\,\rho d}$$
$$\cdot\cos\left\{\left[\frac{nl_1}{\rho a}(1-\cos\rho a)-\frac{n(l_3-l_1)}{\rho d}(1-\cos\rho d)\right]-(V+v')\rho\right\}d\rho. \quad (4)$$

Except when $V=0$, no error is made if $\sin\left(\frac{1}{2}\rho dV\right)/\rho$ is replaced by $dV/2$. For $V=0$, the resulting integral diverges. But (4) is regular at this point, so that we can simply ignore this singularity of the abbreviated integral. Let us further change the variable of integration to $\lambda=\rho d$, and put $a/d=\kappa$. (4) then takes the form

$$I(V)=\frac{e^{-nl_3}}{\pi d}\int_0^\infty e^{nl_1\,\sin\,\kappa\lambda/\kappa\lambda+n(l_3-l_1)\,\sin\,\lambda/\lambda}\cos\left[nl_1\frac{1-\cos\kappa\lambda}{\kappa\lambda}-n(l_3-l_1)\frac{1-\cos\lambda}{\lambda}-\frac{V+v'}{d}\lambda\right]d\lambda. \quad (5)$$

This expression is seen to be independent of the position of the minimum of $f(x)$. But this fact has no physical significance; it results from our choice of equal probabilities for the space distribution of the perturbers.

Expression (5) has been evaluated for different sets of values of the parameters involved, corresponding to different types of $f(x)$. We are reproducing the three (Figs. 1, 2, 3) which seem most interesting. It will be noticed that the integrand in (5) does not vanish for large λ. Nevertheless the range over which graphical integration is necessary is not too large, for as λ increases the integrand becomes a cosine function the contribution of which can be computed. For different values of V, the graphical integrations had to be extended over different ranges, of course. The work is a little tedious, but straightforward.

The order of magnitude of the constants in $f(x)$ is easily found. We know experimentally that the minimum of $f(x)$ lies approximately 10^{-7} cm from the origin. If the pressure is about 37 atm., the number of perturbing molecules per unit volume is 10^{21}, so that $n/L=10^7$. Hence nl_1, or nl_2, is about 1, since $l=x/L$. Values of magnitude unity should therefore be used in calculating (5). The magnitude of d need not be specified, for we shall plot $I(V)$ as a function of V/d and ignore normalization.

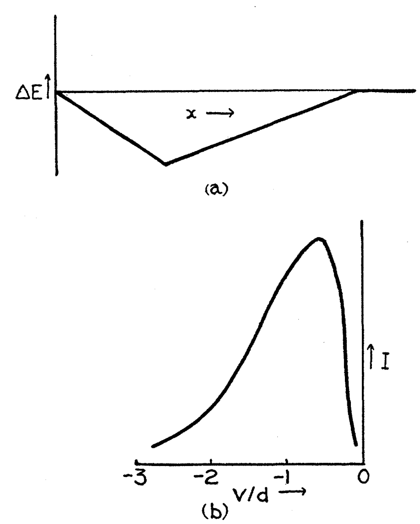

FIG. 1. Curve b represents the contour of a spectral line corresponding to an interaction curve $f(x)$ given by curve a.

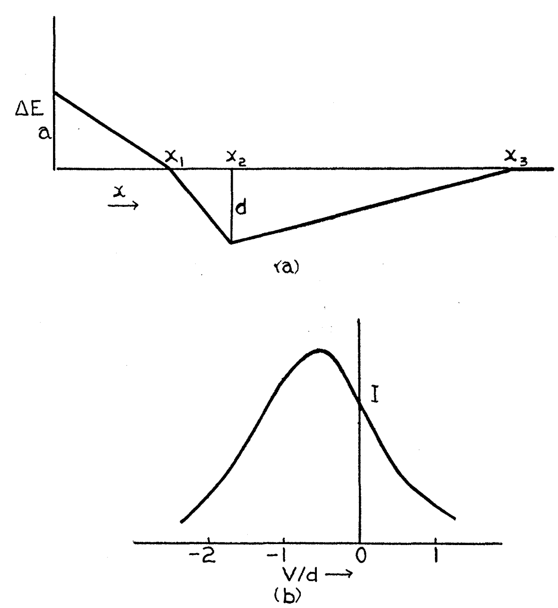

FIG. 2. Curve b represents the contour of a spectral line corresponding to an interaction curve $f(x)$ given by curve a.

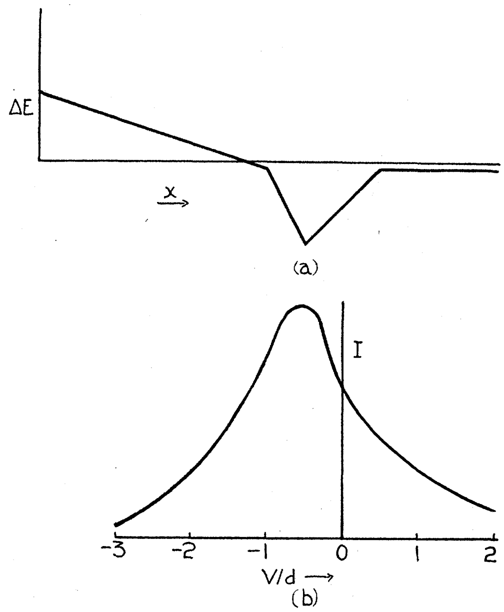

FIG. 3. Curve b represents the contour of a spectral line corresponding to an interaction curve $f(x)$ given by curve a.

Fig. 1 represents a case which seems rather common. We have taken $\kappa=0$, $l_1=0$, $n(l_3-l_1)=2$, so that the energy curve has no positive portion at all. The corresponding spectral line is shifted to the red, strongly broadened to the red. It has no intensities to the blue of the undisplaced position. In reality $f(x)$ has a small positive portion, so that the contour of the line extends a little to the blue of the origin. v has been taken to be 0.

In Fig. 2 the values $\kappa=1$, $nl_1=\frac{1}{2}$, $n(l_3-l_1)=\frac{3}{2}$, $v=0$, have been chosen. $f(x)$ rises above 0; the resulting line is practically symmetrical, but shifted to the red. This case corresponds somewhat to the broadening of Hg 2537 or the D-lines by H_2.

In Fig. 3 the positive portion of $f(x)$ has been taken rather large, the minimum sharp. Here $\kappa=1$, $nl_1=1$, $n(l_3-l_1)=\frac{1}{2}$, $(n/L)v=d$. The spectral line is broadened to the blue, shifted to the red. Füchtbauer and Gössler's[3] observations indicate that in passing from the $7p$ to the $8p$-state of Cs the interaction curves change from the type of Fig. 1 or 2, to that of Fig. 3. This implies an increase in the atomic radius, which should, of course, take place.

While the general character of the curves $f(x)$ here chosen *is* significant, the constant κ has little meaning because of the neglect of the Boltzmann factor. In a real case, the upper curves go up more steeply toward zero. But it must be remembered that, at about the distance of the kinetic theory radius, the lower curve also turns up very strongly, preventing closer approach. The value of $f(x)$ at the origin should therefore be interpreted as the energy difference at the distance of closest approach rather than at $r=0$. It makes no difference in our statistical analysis whether the origin of abscissae in $f(x)$ is taken to be 0 or some finite value.

The shift of the intensity distributions here discussed is given by $(n/L)\int f(x)dx$, hence is proportional to the pressure. To prove this, write in accordance with (1) *et seq.*:

$$I(V)=\frac{L^{-n}}{2\pi}\int_{-\infty}^{\infty}d\rho F(\rho)^n e^{-i(V+v')\rho},$$

$$\bar{V}=\int I(V)VdV=(L^{-n}/2\pi)\int_{-\infty}^{\infty}d\rho F(\rho)^n e^{-iv'\rho}\int_{-\infty}^{\infty}Ve^{-iV\rho}dV$$

$$=\frac{iL^{-n}}{\pi}\lim_{A\to\infty}\int_{-\infty}^{\infty}d\rho F(\rho)^n e^{-iv'\rho}\frac{d}{d\rho}\frac{\sin(A\rho)}{\rho}.$$

If this is integrated by parts, one term vanishes, and the other reduces to

$$-\frac{iL^{-n}}{\pi}\left[\pi\frac{d}{d\rho}\left(F(\rho)^n e^{-iv'\rho}\right)\right]_{\rho=0}=\frac{n}{L}\left[\int\varphi(x)dx-v\right],$$

since, by (3), $F(0)=L$ and $F'(0)=i\int\varphi(x)dx$. Because of the definition of $f(x)\equiv\varphi(x)-v/L$, this is equivalent to the statement above.