Pressure Broadening of Spectral Lines. II

HENRY MARGENAU, *Yale University*

(Received November 29, 1932)

Pressure broadening by foreign gases has been treated in a previous communication on the basis of a statistical analysis of the van der Waals interaction curves. It is now shown that this statistical analysis must necessarily lead to the same result as the more common, but less perspicuous, procedure of expanding the modulated frequencies in a Fourier integral. There is no collision broadening which is not included in the effect previously discussed.—The effect of light modulations by the momentary screening action of absorbing particles is considered.—Extending the former results, we have calculated the distribution of frequencies within a spectral line broadened by foreign pressures, obtaining an approximate closed expression, and an accurate function which can be evaluated graphically. Agreement with experiment on the Hg line 2537A is good, though not entirely unambiguous because of some lack of certainty of the molecular constants of attraction. More significant, perhaps, is the fact that it is possible now to determine the latter from an analysis of the line contour.

§ 1.

THE following considerations are partly an extension of the results obtained in a previous paper[1] (herein referred to as I), with an aim to contribute to the understanding of the fundamental mechanism of pressure broadening. Again we wish to treat with numerical detail only the case of broadening by foreign gases, a phenomenon which is essentially simpler than that of resonance coupling between identical atoms. The theoretical description of the latter does not as yet produce satisfactory agreement with experiment.

A very pleasing account of pressure broadening has been given by Lorentz in terms of classical mechanics. He assumes that, while an atom is being forced to vibrate by the incident light wave (we are choosing the case of absorption), its vibrations are suddenly stopped by collision with other atoms. The spectrum of the electrical oscillations is then no longer sharp; it may be represented by the well-known dispersion curve which has a half width determined by the average number of collisions per second, and hence by the diameter of the colliding structures. The diameter thus calculated is a perfectly clear cut physical concept, and has a definite meaning in atomic kinetics.

In view of quantum mechanics this beautiful explanation has become untenable. The best attempt of transcribing it into modern language invokes the correspondence principle and proceeds as follows: Consider the atom as absorbing or radiating continuously, but with a varying angular frequency $\omega(t)$, a function of the time. This frequency will depend on the energy interactions between the atoms. While the absorbing atom is far from its neighbors, ω will be constant and equal to the normal frequency of the atomic line; on close approach of a perturber it will change. The amplitude of the absorbed frequencies will then be given by a Fourier analysis of $\exp [i\int_0^t \omega(t)dt]$; hence, if $J(\alpha')$ is the amplitude of the angular frequency α',

$$J(\alpha')=\text{const.} \int [\exp (i\int_0^t \omega(\tau)d\tau)]e^{-i\alpha' t}dt. \quad (1)$$

The integration extends over all time. Lorentz' result is now obtained at once by making $\omega(t)$ a step function which has the constant value ω_0 for a long time, then changes abruptly to another constant value, ω_1, and finally returns suddenly to ω_0. In this analysis it is necessary, however, to neglect the contribution of ω_1 to the resulting frequencies and to regard only the change in phase. This procedure also permits a calculation of a definite diameter of collision.

But the modulation of frequencies can certainly not be neglected. Nevertheless the problem at hand may now be solved at least qualitatively

[1] H. Margenau, Phys. Rev. 40, 387 (1932).

by inquiring, if $\omega(\tau)$ is a given continuous function of τ, at what time τ' during the approach of two atoms, the frequency modulation amounted to a phase change of π radians, while again the actual contribution of the varied frequency to the resulting spectrum is neglected. If then the speed of approach is known, this method allows again the computation of a certain distance of approach, corresponding to τ', which has frequently been termed "optical collision diameter."[2] Quite naturally this would be a quantity which, if it be inserted as atomic diameter into Lorentz' formula, produces a half width equal to that observed. But clearly, Lorentz' formula has little meaning in this case, and the "optical diameter" thus computed is a fictitious entity without direct significance in atomic dynamics. Moreover, the separation of the total effect into a phase change and a frequency modulation seems artificial indeed. We desire to show that it is unnecessary.

The validity of Eq. (1) in quantum mechanics would be debatable if it had no stronger support than the correspondence principle. It has been shown by Weisskopf,[3] however, that the probability amplitude of a transition with frequency (α'), if calculated wave mechanically to a first approximation (Wentzel-Brillouin-Kramers method), is given by (1). But for the classical $\omega(\tau)$ one must substitute $(2\pi/h)V(\tau)$, where $V(\tau)$ is the energy difference between corresponding points on the two potential energy curves between which transitions take place. Referring to I, Fig. 1,

$$\omega(\tau)=(2\pi/h)\,V(\tau)=(2\pi/h)[\eta(\tau)-\epsilon(\tau)]. \quad (2)$$

With this value for $\omega(\tau)$, therefore, Eq. (1) should give correct results for the amplitudes if it is rigorously evaluated.

The point of view[4] taken in I appears to be entirely different. The spectrum of the broadened line is not determined from a Fourier analysis of frequencies, but from a statistical analysis of the energy curves. Explicitly, the fundamental hypothesis may be stated most simply as follows (for convenience we confine our remarks to the case of interaction between two atoms only; the generalization to large numbers is considered later): The chance that the energy of transition of the atom lies within the range between $V-\frac{1}{2}dV$ and $V+\frac{1}{2}dV$ is proportional to the length of time which the system spends on that part of curve η or ϵ (I, Fig. 1) whence a transition within this range of energies can occur. In accordance with the Frank-Condon rule, only vertical transitions need be considered. Thus, denoting this chance by $I(V)$,

$$I(V)dV=c\int_V dt, \quad (3)$$

the integration extending only over the range of energies just defined. Strictly, each state should be weighted by the Boltzmann factor, but as a result of I the effect of this modification is not considerable and will be neglected throughout this paper. If the speed of approach of the atoms is nearly uniform during the motion, dt may be replaced by dx in a one-dimensional problem, or in general by an element of volume, as was done in I.

Now

$$(1/\pi)\int_{-\infty}^{\infty}\sin\left(\tfrac{1}{2}xdV\right)e^{i[V-V(t)]x}dx/x=1, \quad (4)$$

if $V-\frac{1}{2}dV\leqq V(t)\leqq V+\frac{1}{2}dV$, otherwise 0. Hence

$$I(V)dV=c\int dt\int\sin\left(\tfrac{1}{2}xdV\right)e^{i[V-V(t)]x}dx/x,$$

where both integrations extend from $-\infty$ to $+\infty$. If during the time of sojourn in the considered energy range a spectral line is emitted, its frequency will lie in the neighborhood of $\alpha=2\pi V/h$. The intensity corresponding to the frequency α is therefore seen to be

$$I(\alpha)d\alpha=c\int\int dtdx\,\sin\left(\tfrac{1}{2}xd\alpha\right)e^{i\alpha x-i\omega(t)x}/x \quad (5)$$

with ω defined by (2). We will now show the equivalence of (1) and (5).

According to (1), the intensity due to frequency α is given by

---

[2] H. Kallmann and F. London, Zeits. f. physik Chemie **2**, 241 (1929); V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).

[3] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).

[4] The same point of view is implied in Weizel's explanation of the asymmetric broadening of the resonance line of He. Cf. W. Weizel, Phys. Rev. **38**, 642 (1931).

$$I(\alpha)d\alpha=\int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2}|J(\alpha')|^2 d\alpha'$$
$$=\int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2}\int\int \exp\left[i\int_0^t \omega(\tau)d\tau -i\int_0^{t'}\omega(\tau)d\tau+i\alpha'(t'-t)\right]dtdt'd\alpha'$$
$$=\int\int dtdt' \exp\left[i\int_0^t \omega(\tau)d\tau -i\int_0^{t'}\omega(\tau)d\tau+i\alpha(t'-t)\right]\frac{\sin\left[\frac{1}{2}d\alpha(t'-t)\right]}{t'-t}.$$

The last integrand is appreciable only where $t'\sim t$. On the other hand, $\omega(\tau)$ is a continuous function which does not change very suddenly. It is therefore permissible to expand the second integral in the exponent as a Taylor series in $(t'-t)$ and retain only the first two terms. Thus

$$I(\alpha)d\alpha=\int\int dtdt' e^{i\alpha(t'-t)-i\omega(t)\cdot(t'-t)} \times \sin\tfrac{1}{2}d\alpha(t'-t)/(t'-t).$$

This is identical with (5) if one variable of integration is changed from $(t'-t)$ to x.

Hence the description of pressure broadening by a statistical analysis of the potential curves must yield the same result as the Fourier analysis of the varying frequency. This result is contrary to some of Weisskopf's[3] statements (and removes his objections to the reasoning of Jablonski).[5] It lends further justification to the considerations of I. Furthermore, ease of generalization and conceptual simplicity would seem to favor the statistical method.

In I we introduced a parameter R_1 (cf. Fig. 1) which was found to be larger than, but comparable to, kinetic theory diameters. This distance is not to be confused with the "optical collision diameters" referred to in this paper, but is, as nearly as it is possible to define such quantities at present, the distance of closest approach of the colliding structures.

The equivalence which we have exhibited also clarifies the question as to the existence of other causes of broadening. The statistical analysis of potential curves takes account of all intermolecular causes of broadening; one must not look for additional effects due to collisions, changes of phase, quenching of the radiation and the like. In particular, quenching as a result of collisions of the second kind should make itself felt in a decrease of the integrated intensity of the spectral line. Traces of it are clearly to be seen in the experiments of Füchtbauer, Joos, and Dinkelacker.[6]—The only broadening effects not included in our treatment are, outside of natural line width, only the Doppler effect, and possibly the intermittence of the exciting radiation caused by sudden screening due to passage of other absorbing atoms through the light path. This latter influence,[7] which we desire to sketch briefly, is certainly absent when a foreign gas without appreciable absorption for the wavelength in question is broadening the line. Hence it is not to be considered in connection with the calculations in I, but it may be important when a gas atom is perturbed by neighbors of its own kind, all of which are absorbing.

§ 2.

Suppose that the radiation falling upon one particular atom is occasionally cut off or diminished by another structure passing through its line of sight. Let the average period of uninterrupted excitation be τ. We suppose that the atom is in its lowest state 1 at $t=0$ and inquire as to the probability that at time t the state k be excited. This probability is $|a_k|^2$, where a_k is the k^{th} coefficient in the development of the wave function perturbed by the radiation, in terms of the unperturbed wave functions. Let us call the latter u_i, and the perturbing potential of the light wave V. Then, by the method of variation of constants, $(h/2\pi i)\dot{a}_k=\sum_i a_i V_{ik}$, V_{ik} being $\int u_k^* V u_i dv$, with $u_i=\psi_i e^{2\pi i E_i t/h}$. Of the a's on the right, neglect all but a_1, as is customary to obtain a first approximation. Putting $V=Aex\sin\omega t$ and integrating in the usual fashion, the result is

$$a_k=\frac{\pi i A e x_{1k}}{h}\left[\frac{e^{-i(\omega_0-\omega)t}-1}{\omega_0-\omega}\right],$$
$$\omega_0=(2\pi/h)(E_k-E_1),$$

[5] A. Jablonski, Zeits. f. Physik **70**, 723 (1931).

[6] Füchtbauer, Joos and Dinkelacker, Ann. d. Physik **71**, 204 (1923).

[7] Cf. H. Margenau, Phys. Rev. **40**, 1036 (1932).

where a term having $\omega_0+\omega$ in the denominator has been neglected. Therefore,

$$|a_k|^2=2\pi^2A^2e^2|x_{1k}|^2/h^2 \times[(1-\cos(\omega_0-\omega)t)/(\omega_0-\omega)^2].$$

Plotting the term in [ ] against ω, the angular frequency of the incident light, it is seen that the "resonance width" of the line depends essentially on t, the time during which the light was allowed to strike the atom. The value of $\Delta\omega\equiv\omega_0-\omega$ for which $|a_k|^2$ reduces to $\frac{1}{2}$ of its maximum value is found by solving the relation

$$\tfrac{1}{2}(t^2/2)=[1-\cos(\Delta\omega\cdot t)]/(\Delta\omega)^2.$$

This gives $\Delta\omega=2.79/t$.

Assuming now $t=\tau$, we find for $2\Delta\nu$, the half width of the line in frequency units,

$$2\Delta\nu=0.89/\tau. \tag{6}$$

It may be of interest to observe that (6) has the same form as the well-known Lorentz formula, if τ is interpreted as the mean time between collisions. The physical cause of the breadth is entirely different, however. The formal analogy is not to be interpreted as logical identity. (6) can also be obtained by writing down a Fourier analysis of an intermittent light train with periods of luminosity τ. But there seems to be no satisfactory way to justify this procedure.

In experiments, such as the broadening of the D-lines by Na vapor, τ will diminish with pressure, and effect (6) is to be taken into consideration.

§ 3.

We now return to the case of broadening by foreign gases with a view to determining the actual shape of a broadened absorption line. First, it is necessary to adapt (3) to the treatment of a large number of perturbing elements. If the Boltzmann factor is neglected and the motion between two collisions is considered uniform, the time integration in (3) must be replaced by an integration over that part of the configuration space of all perturbers in which a transition will have the energy V. Let $r_1\cdots r_n$ be the distances of the n perturbing atoms from the absorbing one, v their total volume. Inserting the correct constant c, (3) then becomes

$$I(V)dV=(4\pi/v)^n\int\cdots\int_V r_1^2r_2^2\cdots r_n^2dr_1\cdots dr_n. \tag{7}$$

Henceforth we shall mean by V not the total energy of transition from curve η to ϵ, but the difference between the latter and V_∞, so that V measures the deviation of the transition energy from its normal amount. This requires no change in the form of (7). V is now the sum of the contributions of all perturbers, each of which is proportional to $1/r^6$. Calling the constant of proportionality β (in the notation of I, $\beta=a-b$), $V(t)=\beta\sum_i(1/r_i^6)$. (7) may again be written as an integral over *all* configuration space if the integrand is multiplied by the Dirichlet factor (4). Then

$$\begin{aligned}I(V)dV&=\frac{1}{\pi}\left(\frac{4\pi}{v}\right)^n\int\cdots\int\int_{-\infty}^{\infty}d\rho\,\frac{\sin(\frac{1}{2}\rho dV)}{\rho}\exp\left[-iV\rho+i\beta\rho\sum_i(1/r_i^6)\right]r_1^2\cdots r_n^2dr_1\cdots dr_n\\&=\frac{1}{\pi}\left(\frac{4\pi}{v}\right)^n\int_{-\infty}^{\infty}\frac{\sin(\frac{1}{2}\rho dV)}{\rho}e^{-iV\rho}\left[\int e^{i\beta\rho/r^6}r^2dr\right]^n d\rho.\end{aligned} \tag{8}$$

The space integrations in (8), for which no limits are stated, extend between R_1, the distance of closest approach, and R defined by $4\pi R^3/3=v$. An examination of the integrand will show that it is permissible to replace $\sin(\frac{1}{2}\rho dV)/\rho$ by $\frac{1}{2}dV$ (in spite of the infinite limits for ρ). Putting $\beta/r^6=E$, and $-(2\pi/3v)(\beta^{\frac{1}{2}}/E^{3/2})=u(E)$, (8) takes the form

$$I(V)dV=\frac{dV}{2\pi}\int_{-\infty}^{\infty}e^{-iV\rho}\left[\int e^{i\rho E}u(E)dE\right]^n d\rho \tag{9}$$

where the integration in [ ] is to be carried from β/R_1^6 to β/R^6. u is of the nature of a statistical weight, and we observe that $\int u(E)dE=1$.[8]

An approximate calculation of (9) which shows

[8] Exactly, it is $1-4\pi R_1^3/3v$.

the line shift but not the asymmetry of the intensity distribution can be made as follows. Call the integral in [ ], $f(\rho)$. Put

$$\int E\cdot u(E)dE=4\pi\beta/3vR_1^3\equiv\bar{E}. \qquad (10)$$

Then, if we define $\varphi(\rho)\equiv e^{-i\bar{E}\rho}\cdot f(\rho)$,

$$I(V)dV=dV/2\pi\int_{-\infty}^{\infty}e^{i(n\bar{E}-V)\rho}[\varphi(\rho)]^n d\rho. \qquad (11)$$

$|\varphi(\rho)|$ is always smaller than const./ρ as follows from its definition. Hence one may expect to approximate (11) by expanding $[\varphi(\rho)]^n$ in powers of ρ. If $F(\rho)=\log\varphi(\rho)$, then

$$[\varphi(\rho)]^n=e^{nF(\rho)}. \qquad (12)$$

But

$$F(\rho)=F(0)+\rho F'(0)+\tfrac{1}{2}\rho^2F''(0)+\cdots.$$

Now $\varphi(0)=1$, $\varphi'(0)=0$, $\varphi''(0)=-4\pi\beta^2/9vR_1^9\equiv-s^2$; therefore $F(0)=0$, $F'(0)=0$, $F''(0)\equiv-s^2$. Putting this in (12), and (12) in (11), we obtain

$$I(V)dV=\frac{dV}{2\pi}\int_{-\infty}^{\infty}e^{i(n\bar{E}-V)\rho}e^{-ns^2\rho^2/2}d\rho$$

$$=\frac{dV}{s(2\pi n)^{\frac{1}{2}}}e^{-(n\bar{E}-V)^2/2ns^2}. \qquad (13)$$

This is a Gaussian distribution with its maximum at $V=n\bar{E}$, i.e., a shift of the maximum of $n\bar{E}$ energy units, or $n\bar{E}/h$ frequency units, which agrees with the results of *I* if the Boltzmann factor is neglected (cf. I, Eq. (24)). The half width corresponding to (13) is given by

$$2\Delta\nu=\frac{1.36}{h}\left(\frac{n}{v}\frac{4\pi}{3}R_1^3\right)^{\frac{1}{2}}\frac{\beta}{R_1^6}. \qquad (14)$$

This formula, of course, cannot be correct since it neglects the actual asymmetry of the distribution, but it gives the orders of magnitude of the experimental half widths[6] quite well and may be used in estimations. (R_1 can be determined independently from the shift, and β may be obtained by the methods of I.) The difference in the broadening effects of the different rare gases found by Kunze[9] is in qualitative agreement with (14).

We shall now carry through a more accurate evaluation of (9). There seems to be no way of expressing it in a closed form; final resort has to be taken to graphical integration. By using the previous notation, (9) may be written

$$I(V)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-iV\rho}[f(\rho)]^n d\rho, \qquad (15)$$

where

$$f(\rho)=-\frac{2\pi}{3v}\beta^{\frac{1}{2}}\int_{\gamma}^{\beta/R^6}\frac{e^{i\rho E}}{E^{3/2}}dE \qquad (16)$$

and where we have used the abbreviation $\beta/R_1^6=\gamma$. Let us also put $\rho\gamma=x$, and $(4\pi/3)R_1^3=v_1$.

Changing the variable of integration in (16) to $\rho E=u$, and integrating by parts, one obtains

$$f(x)=\frac{2\pi}{3v}\left(\frac{\beta x}{\gamma}\right)^{\frac{1}{2}}\left\{2\frac{e^{iu}}{u^{\frac{1}{2}}}\bigg|_x^{xR_1^6/R^6}-2i\int_x^{xR_1^6/R^6}\frac{e^{iu}}{u^{\frac{1}{2}}}du\right\}.$$

$$\doteq 1-\frac{v_1}{v}e^{ix}-i\frac{v_1}{v}x^{\frac{1}{2}}\int_x^0\frac{e^{iu}}{u^{\frac{1}{2}}}du.$$

The remaining integral on the right is a combination of Fresnel integrals, for which tables are available. We use the notation of Jahnke and Emde[10] and find for the last expression

$$f(x)=1-(v_1/v)[(2\pi x)^{\frac{1}{2}}S(x)+\cos x] + i(v_1/v)[(2\pi x)^{\frac{1}{2}}C(x)-\sin x].$$

$|f(x)|<1$ for all x, hence it can be justified to replace $[f(x)]^n$ by

$$\exp[-(nv_1/v)\{(2\pi x)^{\frac{1}{2}}S(x)+\cos x - i(2\pi x)^{\frac{1}{2}}C(x)+i\sin x\}],$$

even under the integral (15), which then becomes

$$I(V)=\frac{1}{2\pi\gamma}\int_{-\infty}^{\infty}\exp\left[-\frac{nv_1}{v}\{(2\pi x)^{\frac{1}{2}}S(x)+\cos x-i(2\pi x)^{\frac{1}{2}}C(x)+i\sin x\}-i\frac{V}{\gamma}x\right]dx.$$

Noting the relations: $C(-x)=iC(x)$, $S(-x)=-iS(x)$, the last expression takes the final form

[9] P. Kunze, Ánn. d. Physik **8**, 500 (1931).

[10] Jahnke and Emde, *Funktionentafeln*, p. 23.

$$I(V)=\frac{1}{\pi\gamma}\int_0^\infty \cos\left[\frac{nv_1}{v}((2\pi x)^{\frac{1}{2}}C(x)-\sin x)-\frac{V}{\gamma}x\right]\times\exp\left[-\frac{nv_1}{v}\{(2\pi x)^{\frac{1}{2}}S(x)+\cos x\}\right]dx. \quad (17)$$

This is no longer a symmetrical distribution. For large V, I takes on small but finite values. If $V\leqq 0$, however, $I=0$, as can best be seen from (9) if it is written

$$I=\frac{1}{2\pi}\int_{-\infty}^\infty d\rho e^{-iV\rho}\int\cdots\int e^{i\rho\cdot(E_1+E_2+\cdots E_n)}\times u(E_1)\cdots u(E_n)dE_1\cdots dE_n.$$

If now the integration over ρ is carried out, the result is

$$\frac{1}{\pi}\int\cdots\int u(E_1)\cdots u(E_n)dE_1\cdots dE_n\cdot\left\{\lim_{A\to\infty}\frac{\sin[A(\sum E-V)]}{\sum E-V}\right\}.$$

Next integrate over E_n. The result will be 0 unless the point $E_n=V-\sum_1^{n-1}E_i$ is included in the range of integration. But all E's are >0, since they lie between β/R_1^6 and β/R^6. Hence the result is different from 0 only when $V>0$.

One can also show by direct calculation that the center of intensity of the line is shifted from 0 to $(nv_1/v)\gamma$, as was also found previously. But this, together with the fact of asymmetry, implies that the shift of the maximum is smaller than that amount. The quantity measured experimentally is the shift of the maximum,[4] and not that of the center of intensity. To this extent the numerical computations in I, where the latter two were considered coincident, require revision.

Experimentally, the intensity does not fall to zero at the position of the undisplaced line. The reason is obvious: Referring to I, Fig. 1, we are neglecting all transitions to the left of R_1. But these are predominantly of larger energy than E at infinite separation. Hence it is clear that our simplified interaction model, in which the inner part of the energy curve is replaced by a straight line, is incapable of producing shifts to the blue, while rendering properly the interactions at larger distances of separation which are responsible for red shifts (in the case of Hg perturbed by gases). Furthermore, the assumption of uniform motion between collisions does particular violence to transitions taking place on the inner portions of the curves. But these idealizations cannot be avoided in a reasonably simple way. Eq. (17) should portray correctly, however, the shift of the maximum and the asymmetries on the red side of the line.

Fig. 1 of this paper shows the result of a graphical integration of (17) for a value of n/v corresponding to an actual experimental case.

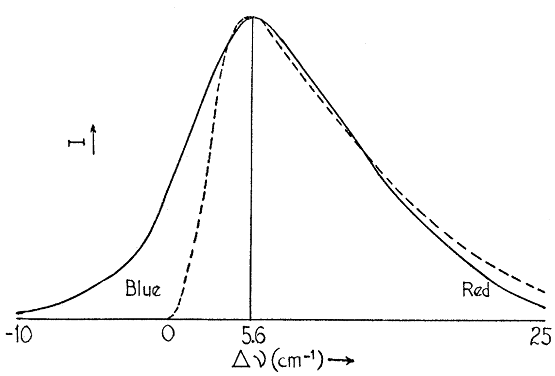

FIG. 1. *Solid curve:* Experimental absorption contour of Hg 2537 broadened by 50 atm. of N_2-pressure. (Füchtbauer, Joos and Dinckelacker,[6] Fig. 5, p. 215.) *Broken curve:* Eq. (17), plotted for the same pressure, with $\beta=47$ volts$\times$A^6,* $R_1=5.6$A.

The result is particularly satisfactory since no great effort has been made in selecting values of R_1 that would produce the best fit. More significant than this agreement, perhaps, is the fact that it is now possible to determine the molecular constants R_1 and β by analyzing the intensity distribution in pressure broadened lines and fitting it by adjusting the constants in (17). This procedure would lead to interesting correlations with other phenomena, when sufficient experimental data are available.

* This value results if in Eq. (19b) of I the sum of the f's for Hg is set equal to 2.7 instead of 2, as was done in the paper. Cf. also footnote 11 of I.