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Pressure Shift and Broadening of Spectral Lines

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The pressure shift of spectral lines, unexplained by the usual theories of pressure broadening, can be adequately treated on the basis of a theory which considers the perturbations produced by neighboring atoms on the two states between which transitions occur. The analysis presented in the paper is directly applicable only to absorption lines, but its consequences are qualitatively correct for emission lines as well. The forces acting on the unexcited atom are the usual van der Waals forces; the perturbations of the excited state are produced by interactions of the same character (dispersion forces) but of different magnitude. The energy increments for both cases can be roughly computed by means of spectroscopic data, which renders possible the evaluations of the mean energies of transitions and hence of pressure shifts. Details are worked out mainly for the shift of λ2537 (Hg) in foreign gases, and are compared with the experimental data of Füchtbauer, Joos, and Dinkelacker. In this case, the energy increments are negative both for the excited and for the normal state of Hg, but larger for the former. Hence there results a red shift, whose magnitude agrees well with observations. The line width produced by the perturbations here considered is an appreciable portion of the total experimental half-width. It is no longer necessary, therefore, to explain the total broadening effect of foreign gases by an appeal to Lorentz collisions. Main results of the theory are: the shift is proportional to the density of the perturbing gas; it is usually to the red, but may, under conditions discussed in the paper, be to shorter wave-lengths; a dependence of the shift on the temperature exists, but is slight at ordinary temperatures; the "standard deviation" of frequencies within the broadened line is proportional to the square root of the density of the perturbing gas.

A SYSTEMATIC discussion of the influence of pressure on the appearance of spectral lines must distinguish at the outset between the cases of emission and absorption. In the former, numerous causes which can neither be well controlled experimentally nor adequately corrected for by theory, such as Stark effects depending on the character and strength of the exciting, discharge, or pole effects, may play an important part in the phenomenon to be studied, while these disturbances are absent if the lines are produced by absorption. This theory is designed, therefore, to describe only the behavior of absorption lines; the possibility of extending its results to emission is only briefly considered.

Previous explanations of pressure shift and broadening, in so far as they are not due to Lorentz collisions, have mainly conceived of the effects in question as Stark effects, caused by the molecules of the gas. Debye, Holtsmark, Stern, and Lenz[1] have developed methods of calculating the width of broadened lines in terms of molecular electric fields. The perturbing structures, in their theory, either are ions, or carry poles (dipoles and quadrupoles) which, as a consequence of their thermal motions, produce a rapidly changing field

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[1] P. Debye, Ann. d. Physik **58**, 577 (1919); Holtsmark, Phys. Zeits. **25**, 82 (1924); O. Stern, Phys. Zeits. **23**, 476 (1922); W. Lenz, Zeits. f. Physik **25**, 308 (1924).

whose mean resultant at the point of the absorbing atom produces a Stark effect, and hence a displacement of energy levels, in the manner of a static field. The validity of this explanation depends essentially on the existence of ions or permanent poles within the perturbing gas. But under conditions in which absorption lines are produced, ions are certainly rare. Moreover, the molecules of many gases which are known to produce both line shift and broadening certainly have no dipole moments. This permits refuge only to the supposition that they carry quadrupoles, a supposition which is safe in so far as it is difficult to verify experimentally. Spherically symmetrical atoms, such as the inert gases, should not produce permanent fields on this basis, and therefore cause no shift; it is well known, however, that they do. Another objection of an exclusive explanation of pressure phenomena by an appeal to Stark effects arises from the observation that lines which show no appreciable Stark effect may be noticeably shifted.

The point of view taken in this paper is indeed a natural one: we inquire as to the perturbing effect of neighboring molecules on the absorbing one, first, when it is in its unexcited state, next when it is excited. If the energy perturbations in the two cases are not equal with regard to sign and magnitude, the frequency of the line absorbed will depend on the configuration of the surrounding molecules, and the calculation of the average frequency of the line, or the dispersion of frequencies within it, is a simple statistical problem. The energy perturbations between molecules in their normal states are those which give rise to van der Waals forces ("dispersion forces"), whose quantum-dynamical significance has been discovered and discussed by F. London[2] and R. Eisenschitz[3] and others. They can be computed to a fair approximation from the intensities of spectral lines of the molecules in question, or from optical dispersion formulae.

In considering the interactions between an excited atom and its neighbors an important distinction must be made. First, the surrounding atoms may be of the same kind as the excited ones. There is then the possibility of resonance between the systems, which occurs whenever the energy of excitation of the one may be absorbed by another. As is well known, this gives rise to strong perturbation energies which appear in the first approximation of the usual (Schrödinger's) scheme of calculation, and which are essentially of the character of dipole interactions depending on the inverse third power of the distance of separation. Their sign may be positive or negative, so that the excited enegy level may be displaced either upward or downward. To this type of perturbation there corresponds the phenomenon of resonance broadening which has been treated by L. Mensing,[4] J. Holtsmark,[5] and J. Frenkel,[6] partly using the older quantum mechanical methods. Resonance broadening is not considered in this paper.

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[2] F. London, Zeits. f. Physik **63,** 245 (1930); Zeits. f. phys. Chem. **B 11,** 222 (1930).

[3] R. Eisenschitz and F. London, Zeits. f. Physik **60,** 491 (1930).

[4] L. Mensing, Zeits. f. Physik **34,** 611 (1925).

[5] Holtsmark, Zeits. f. Physik **34,** 722 (1925); **54,** 761 (1929).

[6] J. Frenkel, Zeits. f. Physik **59,** 198 (1930).

Accordingly, the cases to which the present calculations apply are those in which the perturbing influence is entirely due to a substance different from the absorbing one. This implies that the perturbing atoms or molecules must be very numerous compared to those whose absorption line is studied, so that each of the latter may be thought of as being entirely surrounded by individuals of a different kind. Moreover, it will be supposed that these are always in their normal state. It will therefore be necessary to investigate in some detail the interactions between an excited atom of one kind with unexcited ones of another; in order to make this investigation definite we shall restrict our discussion mainly to instances where the excited atom is in its lowest P-state. This limitation has the advantage of introducing greater simplicity in the analysis, and of covering at the same time most cases of empirical interest. The forces which are called into play under these conditions are of the same character as the dispersion forces mentioned previously, and their evaluation proceeds along the lines of London's papers.

Under these conditions the only cause of pressure broadening beside the one which forms the object of this paper is that known as Lorentz collision broadening.[7] The present description of this phenomenon is in terms of classical physics; its quantum mechanical analogue, which undoubtedly exists, has not been formulated as far as we are aware. Lorentz considers that the impacts of molecules are not completely elastic, so that, speaking in classical terms, the vibratory energy accumulated by an atom in the process of light absorption, is partly converted into heat at the instant of collision. Therefore he assumes that the frequent collisions require the vibratory motion of the electrons to stop at small irregular intervals, and shows that this is equivalent to the presence of a dissipative term in the equation of motion of the electrons. This, in turn, renders the resonance between light wave and electron less sharp and introduces broadening of the absorption line. This action, while in need of being rephrased in current terminology, is still considered capable of explaining, in part at least, the width of spectral lines absorbed under pressure, but it is incompetent to account for pressure shifts.

Minkowski[8] has observed asymmetries in the broadening of the sodium D-lines. In order to explain their presence he assumes, in accordance with a well-known hypothesis of Oldenberg,[8] that kinetic energy may be withdrawn from, or imparted to, a colliding gas atom during the process of light absorption, so that the absorbed frequency may be slightly diminished or increased with reference to its normal value. Thus plausible values for the broadening are found, and the asymmetries, together with their dependence on the molecular weight of the perturbing gas, are well accounted for. An effect of this sort seems indeed very likely, but it probably produces only slight departures from the normal position of the line and is unsuited to explain the relatively large shifts occurring at very high pressures, as its author himself points out. Hence, in the absence of a theory capable of dealing with these shifts, we are

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[7] H. A. Lorentz, The Theory of Electrons, p. 141.

[8] R. Minkowsky, Zeits. f. Physik **55**, 16 (1929).

[9] O. Oldenberg, Zeits. f. Physik **47**, 184 (1928); **51**, 605 (1928).

to look for the perturbations discussed in the present paper to account for their presence, and it will be shown that they do so satisfactorily.

First, attention will be devoted to the energy perturbations which take place between two atoms or molecules, with the object of obtaining the interaction energy as a function of the distance between the centers of the individuals involved. The excited structure is always an atom, but when for brevity the term atom is applied to both, it will be understood that the perturber may be a molecule in its normal state, as will be clear later.

INTERACTIONS

A. Asymptotic interaction between two different atoms, one in a *P* state and the other in an *S* state (normal state).

The classical mutual potential energy of two neutral structures with nuclei a distance r apart and their centers of negative charge at $(x_1y_1z_1)$ and $(x_2y_2z_2)$ respectively, from their nuclei, can be developed as a series whose largest term at great distances of separation is

$$V = e^2(y_1y_2 + z_1z_2 - 2x_1x_2)/r^3 \tag{1}$$

if the x-axis is placed along the line joining the nuclei. Higher terms, corresponding to the classical interaction of quadrupoles and higher poles, will be neglected. The symmetry of the wave mechanical charge distribution causes the first order energy perturbation, which is merely the average of V over the normal charge distribution, to vanish. The second order energy is

$$E_{10} = -\sum_{\alpha\beta}{}' \frac{|V_{10,\alpha\beta}|^2}{E_\alpha - E_1 + F_\beta - F_0} \tag{2}$$

where the E_α's are the energy levels of atom I, E_1 being in particular the energy of the P state; the F_β's denote the energies of atom II, and F_0 is its normal state, considered an S state.

$$V_{10,\alpha\beta} = \int \bar{u}_{\alpha\beta} V u_{10} d\tau = \int V\bar{\psi}_\alpha(1)\bar{\phi}_\beta(2)\psi_1(1)\phi_0(2)d\tau(1)d\tau(2), \tag{3}$$

since the function $u_{\alpha\beta}$ of the composite system, formed of atom I and atom II while very far apart, is simply the product of ψ_α, the ψ-function describing the state of atom I, and ϕ_β, the ψ-function describing the state of atom II. The numbers in ( ) are abbreviations for the coordinates of the atom whose number is stated. Subscripts 0 and 1 denote the S and the P states, respectively.

Writing now, for instance $x_{1\alpha}(1)$ for $\int \bar{\psi}_\alpha(1)x\psi_1(1)d\tau_1$, there results on account of (1) and (3)

$$\begin{aligned} |V_{10,\alpha\beta}|^2 = e^4r^{-6}[&y_{1\alpha}^2(1)y_{0\beta}^2(2) + z_{1\alpha}^2(1)z_{0\beta}^2(2) + 4x_{1\alpha}^2(1)x_{0\beta}^2(2) \\ &+ 2y_{1\alpha}(1)z_{1\alpha}(1)y_{0\beta}(2)z_{0\beta}(2) - 4x_{1\alpha}(1)y_{1\alpha}(1)x_{0\beta}(2)y_{0\beta}(2) \\ &- 4x_{1\alpha}(1)z_{1\alpha}(1)x_{0\beta}(2)z_{0\beta}(2)] \end{aligned} \tag{4}$$

where all squares on the right are understood to be squares of absolute values. More explicitly, if q is one of the coordinates x, y, or z,

$$q_{0\beta}(2) = \int \overline{R}_\beta(\rho) P_l{}^m(\theta) e^{-im\phi} q R_0(\rho) \rho^2 \sin\theta d\rho d\theta d\phi, \tag{5}$$

the R's being the radial functions for atom II,

$$q_{1\alpha}(1) = \int \overline{R}_\alpha(\rho) P_l{}^m(\theta) e^{-im\phi} q R_1(\rho) P_1{}^\mu(\theta) e^{i\mu\phi} \rho^2 \sin\theta d\rho d\theta d\phi. \tag{6}$$

the R's being the radial functions for atom I. The index μ in (6) representing the magnetic quantum number of the P state in question, may take on the values 0, 1, -1.

The denominators in (2) do not depend on the magnetic quantum numbers m of the states characterized by α and β on account of the space degeneracy of the unperturbed states. Hence the summation over the m's, included in that over α and β, may be performed, for any particular energy state, without regard to the denominator of (2). Elementary calculations on the basis of the definition (5) show that

$$\sum_m x_{0\beta} y_{0\beta} = \sum_m x_{0\beta} z_{0\beta} = \sum_m y_{0\beta} z_{0\beta} = 0,$$

also that

$$\sum_m x_{0\beta}{}^2(2) = \sum_m y_{0\beta}{}^2(2) = \sum_m z_{0\beta}{}^2(2) = \rho_{0\beta}{}^2(2) \cdot \tfrac{1}{3} \delta_{l1}.$$

$\rho_{0\beta}(2)$ is the element of the radial matrix for atom II connecting the S-state (0) with the state β. The corresponding results for the coordinate matrices of atom I, one of whose states is the P state, depend on the value of μ. Here again, simple calculations, performed by means of (6), lead to

$$\begin{aligned}
&\sum_m x_{1\alpha}{}^2(1) = \rho_{1\alpha}{}^2(1) \left[\frac{1}{3} \delta_{l0} + \frac{4}{15} \delta_{l2} \right] \\
&\sum_m y_{1\alpha}{}^2(1) = \sum_m z_{1\alpha}{}^2(1) = \rho_{1\alpha}{}^2(1) \cdot \frac{1}{5} \delta_{l2}, \text{ if } \mu = 0; \\
&\sum_m x_{1\alpha}{}^2(1) = \rho_{1\alpha}{}^2(1) \cdot \frac{1}{5} \delta_{l2} \\
&\sum_m y_{1\alpha}{}^2(1) = \sum_m z_{1\alpha}{}^2(1) = \rho_{1\alpha}{}^2(1) \left[\frac{1}{6} \delta_{l0} + \frac{7}{30} \delta_{l2} \right] \text{ if } \mu = \pm 1.
\end{aligned} \tag{7}$$

Expression (4) can now be summed over all magnetic quantum numbers associated with α and with β. It is necessary to distinguish quantum numbers pertaining to the state α (atom I) from those pertaining to the state β (atom II). This can best be done by adding subscripts 1 and 2 respectively; thus m_1 and l_1 refer to the state α, m_2 and l_2 to the state β. By (4) and (7)

$$\begin{aligned}
&\sum_{m_1 m_2} | V_{10,\alpha\beta} |^2 = \frac{e^4}{r^6} \rho_{1\alpha}{}^2(1) \rho_{0\beta}{}^2(2) \left[\frac{22}{45} \delta_{l_1 2} + \frac{4}{9} \delta_{l_1 0} \right] \delta_{l_2 1} \\
&\qquad \text{if } \mu = 0 \\
&\sum_{m_1 m_2} | V_{10,\alpha\beta} |^2 = \frac{e^4}{r^6} \rho_{1\alpha}{}^2(1) \rho_{0\beta}{}^2(2) \left[\frac{19}{45} \delta_{l_1 2} + \frac{1}{9} \delta_{l_1 0} \right] \delta_{l_2 1} \\
&\qquad \text{if } \mu = \pm 1.
\end{aligned} \tag{8}$$

It is convenient to write these results in terms of dispersion-f-values. As is well known, the f-value $f_{\lambda\mu}$ corresponding to the transition from state λ to state μ measures the intensity of that transition. The intensity of a spectral line emitted or absorbed in a transition from one definite initial state to any final state will, however, be proportional to the sum of the f-values connecting the initial state with all the space-degenerate components of the latter, if no external field is applied. Hence it is convenient to define f-values in terms of a summation over the m-values of the final states:

$$f_{kk'} = \frac{8\pi^2 m}{3h^2}(E_{k'} - E_k) \sum_{m'}(x_{kk'}{}^2 + y_{kk'}{}^2 + z_{kk'}{}^2). \tag{9}$$

Thus, for instance,

$$\begin{aligned} f_{1\alpha} &= \frac{8\pi^2 m}{3h^2}(E_\alpha - E_1) \sum_{m_1}\left[x_{1\alpha}{}^2(1) + y_{1\alpha}{}^2(1) + z_{1\alpha}{}^2(1)\right] \\ &= \frac{8\pi^2 m}{3h^2}(E_\alpha - E_1)\rho_{1\alpha}{}^2(1)\left(\tfrac{2}{3}\delta_{l_1 2} + \tfrac{1}{3}\delta_{l_1 0}\right). \end{aligned} \tag{10}$$

The latter expression results if (7) is used.

This result, of course, is independent of the value of μ; i.e. the f-value does not depend on the space orientation of the initial state. Denoting the f-values for atom II by g, we find correspondingly

$$g_{0\beta} = \frac{8\pi^2 m}{3h^2}(F_\beta - F_0)\rho_{0\beta}{}^2(2)\delta_{l_2 1}. \tag{11}$$

(10) shows that it is necessary to distinguish two groups of $f_{1\alpha}$'s, one, in which α is a state with $l_1 = 2$, and the other $l_1 = 0$. All f's belonging to the first group will be called $f_{1\alpha'}$, the others $f_{1\alpha''}$. Thus, in substituting f- and g-values defined by (10) and (11) for the radial matrices in (8), different coefficients have to be used for the two groups of f's. (8) is then introduced into (2) where, accordingly, two separate summations with different coefficients appear. Thus, putting

$$(E_\alpha - E_1)(F_\beta - F_0)(E_\alpha - E_1 + F_\beta - F_0) = D_{\alpha\beta}, \tag{12}$$

we obtain

$$E_{10} = -\frac{1}{r^6}\cdot\frac{3}{4m^2}\left(\frac{he}{2\pi}\right)^4\left\{\frac{11}{5}\sum_{\alpha'\beta}\frac{f_{1\alpha'}g_{0\beta}}{D_{\alpha'\beta}} + 4\sum_{\alpha''\beta}\frac{f_{1\alpha''}g_{0\beta}}{D_{\alpha''\beta}}\right\} \tag{a}$$

$$\text{if } \mu = 0, \tag{13}$$

and

$$E_{10} = -\frac{1}{r^6}\cdot\frac{3}{4m^2}\left(\frac{he}{2\pi}\right)^4\left\{\frac{19}{10}\sum_{\alpha'\beta}\frac{f_{1\alpha'}g_{0\beta}}{D_{\alpha'\beta}} + \sum_{\alpha''\beta}\frac{f_{1\alpha''}g_{0\beta}}{D_{\alpha''\beta}}\right\} \tag{b}$$

$$\text{if } \mu = \pm 1.$$

The summations are now extended only over the non-degenerate states, no longer over the magnetic quantum numbers. These formulae show that the interaction energy between one atom in a P state and another in an S state (spherically symmetrical) depend on the orientation of the former, and that the forces called into play between these atoms are not strictly to be thought of as central forces.

If the P state is the lowest or a metastable state, all energy differences in the denominators of the summation terms in (13) as well as all f's and g's will be positive, so that the various sums are positive. In this case the interaction is greatest when $\mu=0$, that is, when the statistical charge distribution of the atom in the P state has its two maxima on the line through the two interacting atoms. ($(P_1{}^0)^2=\cos^2\theta$, and the polar axis has been chosen coincident with the line joining the atoms.) This state of affairs can be understood classically if the forces are interpreted as caused by polarization. For the P atom represents a quadrupole distribution which, if $\mu=0$, produces a field at the other atom twice as strong as if $\mu=\pm1$. Nevertheless, this analogy seems to have no *general* significance, since it will at once appear that these same forces can no longer be placed on the same footing with polarization forces when the P state is an excited state. Ignoring this possibility for the moment, a rough survey of known f-values and energy levels would indicate that the results of the two summations on the right of (13) are often of the same order of magnitude. In this case, as is seen from (13), the ratio of the maximum to the minimum energy of interaction (or force of attraction) is as much as 2.

Now if the P state is an excited one, so that transitions from it to states of lower energy can occur, some of the terms in the summations of (13) *may* indeed be negative (though they will not be negative in general, since the positive transitions of atom II may make the combined transition one to a state of higher total energy). Cases of this kind will be of interest later. Thus it is not impossible for one, or even both, of the Σ's in question to become negative, hence for the expression on the right of (13) to change sign. This would render the forces between the atoms repulsive, of course, a state of affairs which is no longer compatible with their interpretation as polarization forces. An equally possible case is that in which one of the Σ's in (13), for instance the second, yields a negative result, the first being positive. Then there may result the situation that the forces, attractive for one orientation, become repulsive for another orientation of the atom in the P state. The classical analogue of this situation would be the interaction of permanent multipoles. It is evident from these simple considerations that quantum mechanical "dispersion forces" are capable of acting as substitutes for a considerable variety of classical interactions.

While these detailed questions are of basic interest, it is not possible at present to introduce them into the actual analysis of concrete problems. This would require a much more complete knowledge of f-values, derivable from accurate and systematic absorption data on spectral lines, than we have at present. To continue the discussion it is necessary to proceed in a more summary fashion, namely by averaging over the three values of μ. To be sure, such treatment is not completely justified, even if the analysis is to be applied to the atoms of a gas. For here the strongly attractive states will be statistically favoured because of the appearance of the Boltzmann factor in the thermodynamical probability. It is only for high temperatures that this procedure is free from error. For the conclusions of this paper, however, which do not claim high quantitative precision, the resulting simplification is quite in order.

Taking the average of the values of E_{10} given by (13a) and (13b), and remembering that the statistical weight of (13b) is twice that of (13a), the coefficients in front of the two summations become the same, and the result may be written simply:

$$\bar{E}_{10} = -\frac{1}{r^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{\alpha\beta} \frac{f_{1\alpha}g_{0\beta}}{D_{\alpha\beta}}\,. \tag{14}$$

In fact this formula, which neglects dependence on orientation, describes the interaction between two different atoms with any two states in place of the P and the S state, and may be derived from the intensity rule of Burger and Dorgelo. The relation has been stated in this more general form by London. Thus it would have been possible to arrive at (14) more directly, but this derivation would have obscured noteworthy details of our more special analysis.

B. Asymptotic interaction between two different atoms, both in their normal *S* states.

This problem requires no further scrutiny. The question of averaging is now trivial since no space degeneracy exists. Hence the relation corresponding to (14) may be written in conformity with previous notation

$$E_{00} = -\frac{1}{r^6}\cdot\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{\alpha\beta} \frac{f_{0\alpha}g_{0\beta}}{D_{\alpha\beta}} \tag{15}$$

where E_1, appearing in $D_{\alpha\beta}$, is now to be replaced by E_0.

C. Approximations and numerical examples

As London[10] has pointed out, the summation over the f-values and energy levels in (14) and (15) may in some instances be approximated by the use of static polarizabilities. This is possible if (a) the atom to which the summation relates is in the lowest state and (b) the energy differences between the lowest state and all states, respectively, to which transitions (caused by dipole radiation) can occur are nearly equal. Equivalent to the latter condition is the preponderance of one f-value over all the others. Under these circumstances a certain energy difference, usually in the neighborhood of the ionization energy and determinable from optical dispersion formulae, may be placed as a mean value in front of the summation. This paper will deal with interactions in which atom II is always in its lowest energy state. Moreover, atom II is the atom or molecule (to be treated summarily as an atom in an S state) of a gas. Now for all gases the transition from the lowest state to the next higher state of the stable structure (atom in the case of rare gases,

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[10] F. London, Zeits. f. phys. Chem. **11**, 222 (1930).

otherwise molecule) involves an energy which is an appreciable portion of the ionization energy. This is especially true for rare gases, less so for gases like O_2, etc. Nevertheless we shall be obliged to use mean f-values and mean energy differences for the transitions of II. Except in the case of rare gases, this will introduce considerable errors. Calling the mean energy difference ΔF, in conformity with London's notation, we obtain his formula

$$\overline{E}_{k0} = -\frac{1}{r^6}\frac{3}{2m}\left(\frac{he}{2\pi}\right)^2 p\Delta F \sum_\alpha \frac{f_{k\alpha}}{(E - E_k)(\Delta F + E_\alpha - E_k)} \tag{16}$$

where p is the polarizability of atom or molecule II, and k denotes the initial state of atom I (it will be 1 or 0 in our applications).

It is important to determine the sign of the interaction energy. Clearly, all quantities in front of the summation of (16), including ΔF, are positive. $f_{k\alpha}$ is negative or positive, respectively, according as the difference $(E_\alpha - E_k)$ is negative or positive, so that $f_{k\alpha}/(E_\alpha - E_k)$ is always positive, as may be seen from (9). Hence the sign of each term of the summation depends only on the sign of $(\Delta F + E_\alpha - E_k)$.

Let us now distinguish two cases.

(1) Suppose that $k = 0$, designating the lowest energy state of atom I. Then all the quantities $\Delta F + E_\alpha - E_k$ are positive and E_{00} is negative. It is of course well known that forces between unexcited, neutral structures (van der Waals forces) are attractive at large distances.

(2) Let atom I be excited, so that one or more of the terms $(E_\alpha - E_k)$ are negative.

(a) Then Σ_α will be positive only if $\Delta F > (E_k - E_\alpha)$ for the transitions in which $f_{k\alpha}$ is appreciable, that is, which correspond to intense spectral lines. Suppose this to be the case. It will usually be true when atom I is a metal. Another feature of interest can then also be deduced in a qualitative way by general considerations. Since at least one of the $(E_\alpha - E_k)$ is negative, there will certainly be one term in the summation which is numerically larger, on account of its smaller denominator, than any one of the terms in the corresponding summation of case 1. Furthermore there will be a greater number of large terms in Σ_α. This is seen at once by examining the sum rule of Kuhn and Reiche, which states that, approximately, for any state k

$$\sum_\alpha f_{k\alpha} = Z, \tag{17}$$

Z being the number of optical electrons.[11] Now if k is not the lowest or a metastable state, there will be negative f's as well as positive f's, and con-

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[11] The sum rule is exact only if Z denotes the total number of (extranuclear) electrons in the atom. In this form, however, it is useless, since the transitions due to the inner electrons correspond to numerous unknown ultraviolet and x-ray frequencies. Optical transitions of the type responsible for dispersion and the interactions considered here involve mainly the outer electrons, the f-values of the inner ones being rendered ineffective by the large energy differences appearing in the denominators. It is to be remembered that the procedure in the following applications to the cases of Na and Hg, where Z is taken to be the number of electrons in the outer shell, (1 and 2 respectively) may introduce large errors into the analysis.

sequently $\Sigma_\alpha |f_{k\alpha}| > Z$, while if k denotes the lowest or a metastable state, $\Sigma_\alpha |f_{k\alpha}| = Z$. Collecting these observations we note that $\overline{E}_{k0}$ is a larger negative quantity than in case 1. We shall illustrate this by numerical examples, the results of which are of use in discussing pressure shift phenomena. Ignorance of f-values for higher transitions compels us to make very rough approximations and to rely mainly upon (17). Nevertheless it is possible to explain some interesting details of the pressure effect in a crudely quantitative manner. Case 2b will be defined and considered later. The following examples are best understood if reference is made to term diagrams, such as are found in Grotrian, Graphische Darstellung der Spektren, Vol. II.

α. Let atom I be Na, II the N_2 molecule.[12] For N_2 p is $1.74 \cdot 10^{-24}$, ΔF, in the absence of optical dispersion data, will be taken to be the ionization potential, 17 volts. The transition from the lowest S state to the lowest P state of Na is one of 2.1 electron volts, the corresponding f-value is known to be nearly 1.[13] Since this is by far the strongest transition from this S state all others may be neglected. Hence, if r is measured in angstroms and all energies in volts (we shall adhere to this choice of units in the following formulae and indicate it by writing R for r)

$$E_{00} = -\frac{164 \cdot 10^{24}}{R^6} p \cdot \Delta F \left[\frac{1}{2.1(\Delta F + 2.1)} \right] = -\frac{123}{R^6} \text{ volts.} \tag{18a}$$

If Na is in the $3^2P_{1/2}$ state, there is one possible transition to $3S$ with an f-value nearly equal to 0.5, and numerous possible transitions to higher S and D states. All these will be grouped together to one *mean* transition of approximate energy 2 volts. But then, on account of (17), the f-value corresponding to this composite transition must be greater than 1 by an amount equal to the sum of the f's from $3P$ down to all lower states of a one-electron system, provided that the field in the outer portions of the Na atom is considered as appreciably hydrogenic. But the latter f's sum to about 0.5, as may be seen from Sugiura's work.

$$\overline{E_{10}} \overset{\frown}{=} -\frac{164 \cdot 10^{24}}{R^6} p \cdot \Delta F \left[\frac{1.5}{2.1(\Delta F - 2.1)} + \frac{1.5}{2(\Delta F + 2)} \right] = -\frac{270}{R^6} \text{ volts.} \tag{18b}$$

The value of $\overline{E_{10}}$ when the subscript 1 refers to the other doublet state ($3^2P_{3/2}$) will not be materially different from (18b).

β. Let atom I be Hg, atom II A.

For argon, $p = 1.63 \cdot 10^{-24}$, $\Delta F = 17.5$ volts.[14] If Hg is in its ground state $6\ {}^1S$, there are transitions of appreciable intensity to $6\ {}^3P_1$, $6\ {}^1P$, $7\ {}^1P$ with f-values 0.026, 0.71, 2.27[15] approximately. The corresponding energies are 4.9 volts, 6.7 volts, 8.8 volts. Hence

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[12] Measurements on the pressure shift of the D lines perturbed by N_2 are being made by F. T. Holmes to whom the author is indebted for discussions of the experimental features of pressure shift.

[13] Y. Sugiura, Phil. Mag. (7) **4**, 495 (1927).

[14] Herzfeld and Wolf, Ann. d. Physik **76**, 71 (1925).

[15] Wolfsohn, Zeits. f. Physik **63**, 634 (1930). The last of these f's certainly corresponds to a double excitation and does not truly refer to a 7 P term.

$$E_{00} = -\frac{164\cdot 10^{24}}{R^6}\,p\cdot\Delta F\left[\frac{0.026}{4.9(\Delta F+4.9)}+\frac{0.71}{6.7(\Delta F+6.7)}+\frac{2.27}{8.8(\Delta F+8.8)}\right]$$

$$= -\frac{67}{R^6}\text{ volts.} \qquad (19a)$$

It is seen that the sum rule (17) is not obeyed by the 6 S state of Hg. Nevertheless we shall assume it to be valid for the state 6 $^3P_1$. The result to be obtained may therefore be considerably in error, but it will probably be too small. As under α, many transitions may occur to higher levels from 6 $^3P_1$. We choose as their mean energy 5 volts (which places the center of gravity of the transitions about $\frac{1}{2}$ volt below the ionization potential) and as the corresponding f value 2. The transition to 6 ^1S, whose f value is -0.026 (intercombination between singlet and triplet systems) need not be considered. Therefore

$$\overline{E_{10}} \leqq -\frac{164\cdot 10^{-24}}{R^6}\,p\cdot\Delta F\left[\frac{2}{5(\Delta F+5)}\right] = -\frac{82}{R^6}\text{ volts.} \qquad (19b)$$

If in subsequent discussions we use this value the numerical results must be considered as tentative; but the fact that the coefficient in (19b) is greater than that in (19a) seems well beyond doubt and may also be established by other considerations. Similar reasoning leads to the values given in Table I.

TABLE I. *Interaction of Hg with gas molecules for large distances of separation.* E_{00} *denotes the energy of interaction when both the Hg atom and the gas molecule are in their lowest states.* $\overline{E}_{10}$ *is written for the corresponding quantity when the Hg atom is in the* 6 $^3P_1$ *state.* p *is the polarizability of the gas atom; for* ΔF *cf. Eq. (9).*

	$p\cdot 10^{24}$	ΔF (volts)	$-E_{00}\cdot R^6$(volts) (a)	$-\overline{E}_{10}\cdot R^6$ (volts) (b)
Hg−A	1.63	17.5	67	82
Hg−N_2	1.74	17	71	88
Hg−O_2	1.57	13	58	74
Hg−CO_2	2.9	10	97	129
Hg−H_2	0.81	16.4	32	40

2b. Next it will be necessary to consider the case in which ΔF, the energy difference of the preponderant transition of atom II, is smaller than the difference $E_k - E_\alpha$ of greatest transition probability for atom I. Then the right hand side of (16) will change sign, and the forces of interaction become repulsive. An example of this type is afforded by the interaction of a Na atom (I) with a K atom (II). The state of affairs is now more easily described by using formulae (15) and (14). If both Na and K are in their lowest S states the only transitions which need be considered are those to 3 ^2P and 4 ^2P respectively, the corresponding f values being practically 1. Hence

$$E_{00} = -\frac{17500}{R^6}\left[\frac{1}{2.1\cdot 1.6(2.1+1.6)}\right] \doteq -\frac{1400}{R^6}\text{ volts.} \qquad (20a)$$

The transitions of Na from the state $3\ ^2P_{3/2}$ will be dealt with in the same approximate manner as previously (cf. Eq. 18b). Thus, if the Na atom is excited ($3\ ^2P_1$) and the K atom in its lowest state, the interaction energy is

$$\begin{aligned}\overline{E_{10}} &\cong -\frac{17500}{R^6}\left[\frac{0.5}{2.1\cdot 1.6(-2.1+1.6)}+\frac{1.5}{2\cdot 1.6(2+1.6)}\right]\\ &\doteq +\frac{3500}{R^6}\text{ volts.}\end{aligned} \tag{20b}$$

It must be emphasized that these numerical answers, as well as all equations for interaction energies in this paper, are true only for large distances R since no exchange phenomena have been taken into account. But it is to be expected, and will indeed be borne out by our results, that the interactions which are responsible for the behavior of spectral lines here considered take place at distances of separation at which the expressions developed are at least approximately valid. To find the lower limit of R at which they cease to be applicable one merely needs to remember that the perturbation scheme here employed breaks down when the perturbed energies become comparable in magnitude to the differences between the unperturbed energy levels. Since these are usually a few electron volts it is seen that the numerical results from (18) to (20) have meaning as long as $R \gg A^{1/6}$, A being the numerical coefficients of $1/R^6$. (R is in A-units.) Consequently (20a) and (20b) certainly fail at distances of the order of 5 or 6A, a fact which may be regarded as due to the high polarizability of metallic atoms. At a closer approach of the two structures their internal condition would be strongly modified.

In concluding this section the author wishes to express his appreciation of valuable suggestions and criticisms offered to him by Professor Van Vleck in connection with the use of f values.

STATISTICAL CONSIDERATIONS

In order to simplify the statistical analysis four major assumptions will be made:

1. Atom I is surrounded only by individuals of type II. This will restrict the validity of the results to cases in which the pressure of the absorbing substance is small compared to that of the perturbing gas.

2. The mutual attractions between structures II will be neglected in order to avoid irrelevant calculations, a simplification which does not affect the result through the order of terms which we are retaining.

3. Internal electronic changes of atom I, caused by absorption of light, occur adiabatically with respect to its surroundings. They may be thought of as taking place so rapidly, for instance, that the configuration of the neighbors can not readjust itself until after the process of absorption is completed. The extent to which this assumption is justified is difficult to estimate independently of the results to which it leads. Nevertheless it would seem a plausible approximation to the actual state of affairs.

4. The transition probability of atom I is independent of the configuration of the perturbing atoms. Referring to Fig. 1, transitions between the curves ϵ and η are equally likely regardless of where they take place. This assumption is permissible since the energy variations along the curves are small compared to those encountered in band spectroscopy. Possible vibrational levels, and such refinements as the application of the Franck-Condon principle, will be ignored.

Suppose atom I, in its lowest state, to be at the origin of space coordinates, and let it be surrounded by N atoms of type II, situated at $r_1 \cdots r_N$. Reckoning the condition in which all r's are infinite as the zero level of energy, and writing $\epsilon(r_i)$ for the interaction energy of I with the ith atom of type II, the energy of this configuration is $\Sigma_i \epsilon(r_i)$. If I is suddenly excited to a P state whose unperturbed energy is E, then the energy of the configuration immediately after this transition will be $E + \Sigma_i \eta(r_i)$, where $\eta(r_i)$ is written for the interaction energy of I in its excited state with the ith atom of type II. Thus the actual energy difference Δ corresponding to this transition is

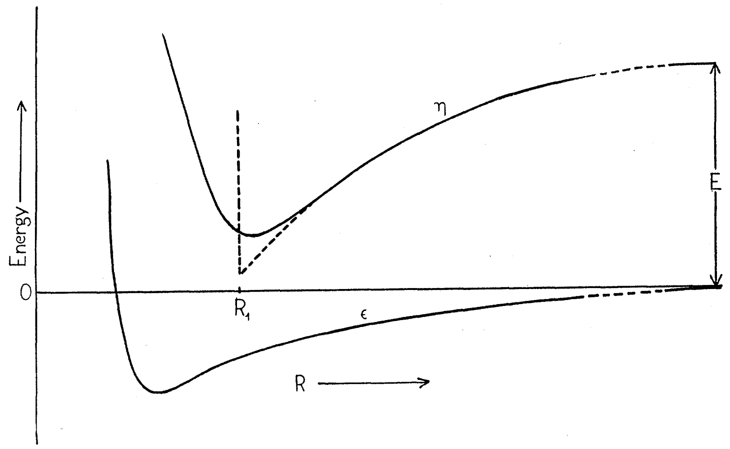

Fig. 1. η = interaction energy of Hg-A when Hg is in the 6^3P_1, a in its normal state. ϵ = interaction energy of Hg-A when both are in their lowest state (van der Waals energy). Dotted curve corresponds to the simplified model here chosen.

$$\Delta(r_1 \cdots r_N) = E + \sum_i [\eta(r_i) - \epsilon(r_i)] \tag{21}$$

But the statistical weight of this space configuration is $e^{-\Sigma_i \epsilon(i)/kT} d\Omega$, where $d\Omega$ is an element of 3 N-dimensional configuration space. For the mean energy of all such transitions one obtains, therefore,

$$\bar{\Delta} = \frac{\int e^{-\Sigma_i \epsilon(r_i)/kT} \left\{ E + \sum_i [\eta(r_i) - \epsilon(r_i)] \right\} d\Omega}{\int e^{-\Sigma_i \epsilon(r_i)/kT} d\Omega} \cdot \tag{22}$$

The integration in the denominator is performed over the space of each individual separately and yields approximately V^N, V being the total volume of the assembly; for $\epsilon(r)$ is known to be different from zero only in a very small sphere about the origin, so that in the remainder of the volume of each individual the integrand is 1. A reduction of the numerator is easily carried out, since every one of the N term in the summation makes the same contribution $V^{N-1}\int e^{-\epsilon(r)/kT}[\eta(r)-\epsilon(r)]\,d\omega$, $d\omega$ being the element of ordinary space. Hence (22) takes the simple form

$$\bar{\Delta} = E + (N/V)\int e^{-\epsilon(r)/kT}[\eta(r) - \epsilon(r)]d\omega. \tag{23}$$

Clearly, the second part of this expression is the energy shift of the spectral line absorbed by atom I; on the wave-length scale it is to the blue when the term is positive. (23) shows that the shift is generally proportional to the density of the perturbing gas, which is the result found experimentally by Füchtbauer, Joos, and Dinkellacker,[16] with whose work this theory will be mainly compared. Hereafter their paper will be referred to as F. J. D. For large values of r, the quantities η and ϵ are identical with $\overline{E}_{10}$ and E_{00} of the preceding section. (R and r denote the same quantity; we are writing R when the distance is measured in A-units.) The probable course of η and ϵ over the total range of distances of separation is qualitatively illustrated in Fig. 1, describing the effect of an argon atom, for instance, upon the 6 S and the 6 $^3P_1$ state of mercury, respectively. The reason for placing the minimum of the upper curve to the right of that in the lower is of course to be seen in the fact, that, in terms of the kinetic theory, the excited Hg atom has a larger "diameter" than the normal atom. (It is for the same reason that R_1, to be defined presently, should be greater than the gas kinetic diameter.)

The further considerations will be applied to a model which may be expected to represent the actual situation fairly closely: We shall suppose that η may be replaced by $\overline{E}_{10}$ for the range from $R=R_1$ to $R=\infty$, and that it suddenly becomes infinite at R_1 and remains so for smaller distances. This is equivalent to a substitution of the dotted curve for η in Fig. 1. Energy transitions during which any $R<R_1$ are then impossible, and the statistical weight zero may be assigned to all Δ's for which any one argument is smaller than R_1. This supposition precludes the possibility of calculating the accurate intensity distribution within the shifted line, and permits only a qualitative estimate of the line width, as will be shown. It has been seen that the asymptotic interaction energies vary as R^{-6}. Let us denote $\overline{E}_{10}$ by $-b/R^6$ and E_{00} by $-a/R^6$. Then, with the premises just discussed,

$$\eta(r) - \epsilon(r) = (a - b)/r^6 = (b - a)E_{00}/a \text{ if } R > R_1.$$

Hence the energy shift, by (23), is seen to be

$$D = 4\pi\frac{b - a}{a}\cdot\frac{N}{V}\int_{r_1}^{\infty} E_{00}e^{-E_{00}/kT}r^2dr, \tag{24}$$

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[16] Chr. Füchtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 204 (1923).

which, when r is expressed in A and E_{00} in volts, may be written as a wave-length shift:

$$\Delta\lambda = 8100\lambda^2 4\pi \cdot \frac{a-b}{a} \cdot \frac{N}{V} \cdot 10^{-32} \int_{R_1}^{\infty} E_{00} e^{-E_{00}/kT} R^2 dR. \tag{25}$$

λ is the wave-length of the displaced line in A, and the shift is to the red when $\Delta\lambda$ is positive.

COMPARISON WITH EXPERIMENT

Many references to pressure shifts are to be found in the literature, but the experimental conditions are frequently such that an adequate theoretical description of the situation can not be made. The experiments of F. J. D., however, present a very interesting set of data to which our considerations may at once be applied. They have measured intensity distribution and shift of the Hg line 2537A absorbed while the Hg vapor was perturbed by different gases at high pressures (10–50 atm.). The straightforward test of the theory would be to evaluate (25) and compare the results with their experimental data. However, R_1 is a parameter concerning the exact magnitude of which there is considerable doubt. Hence it seems more appropriate to choose R_1 so that the value of (25) agrees with the experimental shift. R_1 should then be somewhat larger than the gas kinetic diameter of Hg, if this theory suffices to explain the shift. (25) may be computed graphically; indeed in some cases $e^{-E_{00}kT}$ may be replaced by 1 and the integral computed directly. R_1 means, crudely speaking, the distance of closest approach between the excited Hg-atom and its perturber. The value of R_1, which may thus be computed from the pressure shift, is of some independent interest in other respects. It should be remarked that, within a plausible range of values, the numerical dependence of R_1 upon the choice of b_{10} is such that R_1 is approximately proportional to b_{10}. Table II shows the results. In the first place it is worthy of note that R_1 is of the correct order of magnitude at all, a feature which confirms the qualitative correctness of the considerations here presented. Moreover, for all gases but H_2 the calculated values of R_1 arrange themselves in

TABLE II. *$\Delta\lambda$ is the pressure shift per atmosphere observed by Füchtbauer, Joos, and Dinkelacker, R_1 the distance of closest approach between the excited Hg-atom and its perturber, as caclulated from $\Delta\lambda$ by the present theory. d is the van der Waals diameter of the perturbing atom, and σ the value of the distance between centers at collision, evaluated by means of Lorentz' theory of collision broadening.*[17]

Perturbing gas	$\Delta\lambda$	R_1	B_0	d	σ
A	0.0088	4.8 A	39	3.13 A	9.44 A
O_2	.0079	5.0	46	3.32	8.07
N_2	.0056	5.6	50	3.41	8.05
CO_2	.0078	6.2	105	4.36	11.2
H_2	.0042	4.9	21	2.55	5.27

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[17] $\Delta\lambda$ is not the mean shift per relative density 1, as tabulated by F. J. D. on page 225; it is computed from their lowest pressures only. The slight empirical deviation from a linear relation which takes place at very high pressures is considered to depend on causes not included in the theory.

the order of the van der Waals diameters of their molecules, which have been computed from the experimental values of B_0 given by Beattie and Bridgeman.[18] ($d = [3B_0/2\pi N]^{1/3}$, with $N = 6.06 \cdot 10^{23}$ mol.$^{-1}$) The fact that H_2 violates this order is confirmatory rather than detractive, for H_2 is misbehaved in all similar instances.[19] We shall return to this point. Calculations on H_2O, for which experimental data are also given by F. J. and D., have been omitted since our method would be inadequate in so far as it neglects the interactions of the permanent dipoles and quadrupoles, which H_2O molecules are known to carry.

To our knowledge, there are no quantitative experimental data with reference to the pressure shift of the sodium D lines with which calculations similar to the foregoing ones could be compared. There appear to be some empirical data showing that D_2 is shifted more strongly than D_1.[20] The present theory predicts equal shifts, as the remark following Eq. (18b) implies. Further experimental work on this point would be interesting.

Most of the known pressure shifts are to be red.[21] The opinion has been expressed that blue shifts can not occur. Our analysis enables us to settle this point; it demonstrates the possibility of pressure shifts to the blue. Their occurrence is clearly seen to depend on the relative spacing of the energy levels of the two interacting structures, that is on the condition previously designated as 2b. If this condition is to be satisfied the energy differences between the normal state of the perturbing molecule and that state to which transitions are most likely to occur must be smaller than the difference corresponding to the spectral line absorbed. If the latter is the resonance line of the element whose f value is large compared to that of other transitions, then it is usually sufficient that the strongest transitions of the perturbing substance be of lower frequency, if a blue shift is to be observed. This explains at once why blue shifts are infrequent. The resonance lines with which one can work most conveniently are those of metals, since their wave-lengths fall in a domain which is spectroscopically easy to reach. The perturbing substance must necessarily be a gas, and most gases have ionizing potentials above 10 volts, so that their strongest transitions, or the composite transition previously denoted by ΔF, presumably correspond to wave-lengths in the far ultraviolet. One might well expect, however, to find blue shifts in the case of ultraviolet lines if the perturbing gas is one of relatively low ionizing potential. The Hg lines 1850A would appear to be of some promise in this respect. The details can be worked out for each individual perturber after the fashion of the previous computations.

A theoretically clear cut example of this type is afforded by the pressure shift of the D lines with K vapor as the perturbing agent, as is seen from Equations (20a) and (20b). $\overline{E}_{10}$ is positive in this case, so that η in Fig. 1 would be curved upward. Use of Eq. (20) shows the blue shift to be quite

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[18] Beattie and Bridgeman, Zeits. f. Phsyik **62,** 95 (1930).

[19] Cf., for example, H. Margenau, Phys. Rev. **38,** 365 (1931); **36,** 1782 (1930).

[20] Cf. C. C. Kiess, J. O. S. A. **18,** 169 (1929).

[21] Cf. Humphreys and Mohler, Astrophys. J. **3,** 114 (1896).

large, even if a large value of R_1 is assumed. But in carrying out the experiment, as was attempted in the manner of a preliminary survey by Prof. W. W. Watson and the author, one meets with appreciable difficulties. In the first place, sufficiently high pressures of K vapor can not be obtained without using high temperatures which bring out overlapping absorption bands. These not only obscure the effect to be observed, but also invalidate the theory in so far as they give evidence of the existence of perturbing structures whose transition probabilities are not considered. Furthermore, at higher temperatures the Na atoms present as an impurity in K produce resonance broadening in the D lines which is sufficient to obliterate the shift. Nevertheless, the experiment does not appear to be hopeless if, for instance, low temperatures and pressures are used and interferometer methods employed.

Large pressure shifts are to be expected when the absorbing and the perturbing atom are capable of strong transitions of nearly equal frequencies. This is at once inferred from (14), $D_{\alpha\beta}$ becoming small for one of the terms in this case; it is to be interpreted as an approach to resonance coupling.

Finally, the dependence of the shift on the temperature of the perturbing agent merits attention, for this, too, appears to have been a doubtful point. The temperature enters into the shift through the Boltzmann factor in the integrand of Eq. (25). Consider again Table II. One can easily convince himself that, even at values of R of the order of 5A, E_{00}/kT is smaller than $\frac{1}{4}$ at ordinary temperatures and becomes rapidly insignificant for greater R's. Hence, though the shift is definitely dependent on the temperature, this dependence is very slight at those temperatures at which pressure shifts of absorption lines are usually determined. Differentiating (27) with respect to T, and writing ϵ for E_{00},

$$\frac{1}{\Delta\lambda}\,\frac{\partial(\Delta\lambda)}{\partial T} = \frac{1}{kT^2}\,\frac{\displaystyle\int_{R_1}^{\infty}\epsilon^2 e^{-\epsilon/kT}R^2dR}{\displaystyle\int_{R_1}^{\infty}\epsilon e^{-\epsilon/kT}R^2dR} \doteq -\frac{1}{3kT^2}\,\frac{a}{R_1{}^6}\,. \tag{26}$$

Here again the theory exposes itself to experimental verification.

LINE WIDTH

In dealing with the width of an absorption line we are considering the effect of at least three causes: Doppler effect, Lorentz' intermittent excitation, and the perturbations discussed in this paper. The Doppler broadening is independent of the pressure and given by the formula

$$\Delta\nu_D = 7.16\nu(T/M)^{1/2}\cdot 10^{-7},$$

where M is the molecular weight of the absorbing substance. For Hg at the temperatures used in the experiments of F. J. D., $\Delta\nu_D$ is 0.034 cm^{-1}, a quantity that is inappreciable in comparison with the observed values of $\Delta\nu$, ranging about 6 cm^{-1}. The Lorentz effect, given by the formula

$$\Delta\nu_L = Z/\pi,$$

where Z is the number of impacts per second of the absorbing molecules, has usually been called upon to explain the total line width. There is no doubt, however, that the perturbations to which this paper is devoted account for a large portion, if not all, of the broadening.

The simple model used in this work does not permit us to deal very satisfactorily with the question of pressure broadening since it does not render properly the intensity distribution within the spectral line. The details of this distribution may be essentially distorted by our substitution of the dotted line for curve η in Fig. 1. Hence it is not possible to explain by this theory the interesting asymmetries in the intensities of the D-lines absorbed under pressure, as observed by Minkowski[22] and others. It is certain, however, that the incongruous trends of the real curves ϵ and η would in general cause asymmetries to appear. But we do not wish to offer this as an alternative to Minkowski's explanation, which appeals to the simultaneous occurrence of absorption and collision; probably both of these causes will have to be considered.

The experimental measure of pressure broadening is the "half-width" of the line. This is known numerically from the work of F. J. D. and many others. As pointed out, Lorentz' theory of collision broadening, while incapable of accounting for a shift of the maximum, does enlable a calculation of the diameter of closest approach, σ, between the colliding structures. This quantity would be somewhat analogous to the R_1 of Table II, and may be compared with it. We are therefore tabulating σ, as calculated by kinetic theory,[23] in the last column of Table II. The smaller values of R_1 which the present theory provides are evidently more satisfactory, for it could hardly be supposed that the "diameter" of an excited Hg atom in an impact with a CO_2 molecule is of the order of 18A when in its normal state it is only 3.6A.

The "half-width" of a line has been found by F. J. D. to be proportional to the pressure. It is difficult to correlate the experimental half-width with a definite feature of our model. Yet some interesting information may be derived by calculating the statistical dispersion ("Streuung") s^2 of the frequencies within the line. Putting as before $\eta = -b/r^6$, $\epsilon = -a/r^6$, and writing for convenience

$$c = (a - b)/a, \quad U = \sum_{i=1}^{N} \epsilon(r_i), \tag{27}$$

the dispersion of energies within the absorption line is, by definition,

$$s^2 = \frac{\int (cU - D)^2 e^{-U/kT} d\Omega}{\int e^{-U/kT} d\Omega} \cdot \tag{28}$$

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[22] R. Minkowski, Zeits. f. Physik **55**, 16 (1929). Cf. also M. W. Zemansky, Phys. Rev. **36**, 219 (1930).

[23] Values taken from Zemansky, Phys. Rev. **36**, 219 (1930).

On account of (22), etc.,

$$D = \frac{\int cUe^{-U/kT}d\Omega}{\int e^{-U/kT}d\Omega}\cdot \tag{29}$$

Hence (28) becomes on expanding

$$s^2 = \frac{\int c^2U^2e^{-U/kT}d\Omega}{\int e^{-U/kT}d\Omega} - D^2. \tag{30}$$

Next replace U^2 by its value according to (27) and perform the integration in the numerator. The integrand is $c^2\sum_i\epsilon^2(r_i)+c^2\sum_{i\neq j}\sum_j\epsilon(r_i)\ \epsilon(r_i)$. As previously, $d\Omega$ is the product of the elements of space of all N perturbing molecules. Each of the terms of $c^2\sum_{i\neq j}\sum_j\epsilon(r_i)\ \epsilon(r_j)$ contributes to the integral the same value $c^2V^{N-2}[\epsilon(r)e^{-\epsilon(r)/kT}]^2$, and since there are altogether $N(N-1)$ terms the total contribution of the second sum will be

$$\frac{N^2}{V^2}V^N\left[\int \epsilon(r)e^{-\epsilon(r)/kT}d\Omega\right]^2 = V^ND^2$$

because of (24), and since $N-1$ may be replaced by N, N being very large. But the denominator of (30) has the value V^N, as pointed out before, so that

$$s^2 = \frac{c^2}{V^N}\int \sum_i\epsilon^2(r_i)e^{-U/kT}d\Omega = 4\pi c^2\frac{N}{V}\int_{R_1}^{\infty}\epsilon^2(r)e^{-\epsilon(r)/kT}r^2dr. \tag{31}$$

Thus it has been shown that the statistical dispersion of energies within the absorption line, caused by perturbations alone, is proportional to the density of the perturbing gas, or, roughly, to its pressure. The same is true, of course, of the dispersion of wave-lengths.

This proportionality is disturbed if the "standard deviation" s is regarded as determining the perturbation breadth of the line. As mentioned before, there is no definite criterion for this choice as long as the accurate distribution is unknown. It is clear, however, that the standard deviation should agree in numerical magnitude with the line widths if allowance is made for other causes of broadening. Since s does not vary linearly with the pressure, we can not expect perturbation broadening to be a constant fraction of the total line width over the complete pressure range. Computing it for the example of argon as the perturbing gas and choosing a pressure of 20 atm., we find

$$s \leqq (4\pi N/9V)^{1/2}\cdot 10^{-12}(a-b)/R_1^{9/2} = 3.7\cdot 10^{-4}.$$

This corresponds to a $\Delta\nu$ of 3 cm^{-1}, as against F. J. D.'s half-width of 7 cm^{-1}. For the other gases, the disparity is slightly greater, the computed standard deviation being always smaller than the experimental half-width. This state of affairs may be regarded as satisfactory. Moreover, if the remainder of the line width were considered as due to Lorentz broadening in the classical manner and σ computed from it, there would result better agreement with our values of R_1.[23a]

The question arises as to how the pressure shift and broadening of emission lines is to be treated. A systematic discussion of this problem is difficult since the statistical condition of the gas in which the emission occurs is in general not a steady one, particularly when excitation is produced by strong electrical discharges or thermal activation. If we suppose, however, that the number of excited atoms at any time is small compared to the number of perturbing atoms, and the latter are all in their normal state, which will be true umder proper experimental conditions, then the statistical analysis depends mainly on the life time of the excited state. In this respect, two limiting cases must be distinguished.

(1) The life time of the excited state may be so large that statistical equilibrium between the excited atom and its perturbers is established before emission takes place. The statistical weight of any space configuration is then $e^{-\Sigma_i\eta(r_i)/kT}$ instead of $e^{-\Sigma_i\epsilon(r_i)/kT}$ which was used in the preceding discussion. Consequently, formulae (25) and (31) are applicable if in the Boltzmann factor E_{00} is replaced by $\overline{E}_{10}$.

(2) Emission occurs immediately after excitation, so that the statistical distribution is always determined by the forces between the unexcited structures. In this case, formulae (25) and (31) apply as they are stated.

In either case will the results of the present analysis be a qualitative guide. Nothing can be said in general, however, about the shift of lines which are due to transitions between higher states, where the forces of interaction may become very complex.

CRITIQUE AND SUMMARY

Aside from the necessary numerical uncertainties in the coefficients of the interaction energies there is a valid objection against the method of calculation employed in this paper. In solving the wave mechanical perturbation problem the distance between the interacting structures has been treated as a fixed parameter. Then quantum dynamical reasoning has been abandoned, and the remainder of the problem has been solved by the method of classical statistics. We are, of course, forced to adopt such an inconsistent treatment because of the difficulties which, at present, stand in the way of a quantum dynamical description of a large assembly of systems coupled by forces. It should be remembered, however, that this critique applies to all the usual treatments of similar problems, such as the calculation of virial coefficients and the like.

The method is properly employed only as long as the thermal motion of the molecules is slow compared to the secular changes which the internal structure of the molecules undergoes as a result of the interactions. It is in-

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[23a] *Note added in proof:* The question as to the existence of such an additional effect and its quantum mechanical interpretation will be considered in a later communication.

structive to carry this idea a little further and compare the various gases in this respect. Let us choose the time t during which a molecule in its thermal motion passes through a distance equal to its own gas kinetic diameter as a measure of its slowness, and compare it with τ, the period of secular variations. The magnitude of τ may be obtained from the uncertainty relation: $\Delta E \cdot \tau = h/2\pi$, where ΔE is the energy of perturbation. For it we shall substitute b/R_1^6, the energy at the closest distance of approach, referred to the collisions of Hg with a gas molecule. (Cf. Tables I and II.) Thus the values shown in Table III are found:

TABLE III.

	$t \cdot 10^{13}$ (sec.)	$\tau \cdot 10^{13}$ (sec.)	τ/t
A	7	0.97	0.14
N_2	6.3	2.2	.35
O_2	6.5	1.3	.20
CO_2	10	2.9	.29
H_2	1.2	2.2	1.9

The magnitude of τ/t shows that in all cases we are working in a critical region, and that the approximation should be much worse for H_2 than for the other substances. Indeed we are inclined to regard this large value of τ/t, which is obtained for He as well as for H_2, as indicating the unsuitability of this method for problems of the type here discussed.

The neglect of exchange phenomena in the calculation of interactions restricts formulae (14) and (16) to cases in which valence forces are absent. For if a chemical compound could be formed, the curve η in Fig. 1 would be entirely incorrect at small values of R. There would then in general be more than one mode of interaction, and at least one of them would correspond to a curve which, instead of turning upward as shown in the figure, continues downward to a much stronger minimum at a shorter distance of separation. Na and K are known to form a molecule. Hence, if the chemical affinity is sufficiently great it may be that our considerations regarding the shift of the D lines caused by perturbing K atoms are not appropriate.

To summarize: the phenomenon of pressure shift is to be understood as produced by perturbations of the energy levels of the absorbing or emitting molecule. The energy of perturbation is caused by the interactions of the rapid internal motions of the structures, the forces being of the type designated as "dispersion" forces by London, and different from the forces of static polarization. They vary with R^{-7}, R being the distance between interacting centers.

The theory is capable of explaining the numerical magnitudes of the shifts observed experimentally within the margin set by the uncertainty of other quantities involved in the calculation. It shows the shift to be proportional to the pressure of the perturbing gas, as found empirically. It explains furthermore why most of the observed shifts are to the red, and suggests the occurrence of blue shifts in cases which have not been investigated. The direction of the shift depends primarily on the relative spacing of the energy levels of the interacting structures. The discussion is restricted, however, to the effect upon lines due to transitions between the lowest *S* and the lowest *P* state.

The width of the line produced by the perturbations in question is an appreciable portion of the measured half-width, provided that the standard deviation of frequencies within the line is taken as a measure of the perturbation width. This standard deviation increases with the square root of the pressure. As a result, it is no longer necessary to hold classical Lorentz broadening responsible for the total line width, a procedure which has been shown to lead to improbably large collision diameters in some instances. The considerations are immediately applicable only to absorption lines; but the results should, under suitable excitation conditions, apply roughly to emission lines as well.