METHODS FOR DETERMINING TRANSITION PROBABILITIES FROM LINE ABSORPTION

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ABSTRACT

Computation of quantum transition probabilities from measurements of absorption in spectral lines.—The various steps are discussed, practical methods being given for performing the calculations. The absorption coefficient can be found by the exponential law from knowledge of the intensity of absorbed and non-absorbed light. In doing this, the intensity curve must be corrected for slit width, and a simple method for this, applicable when there is good resolution, is given. Also methods are given for fitting constants of the ordinary formula for absorption coefficient in a spectral line to the observed data. Several points connected with half breadth, failure of the exponential law with poor resolution, are discussed and finally formulas are given for finding the atomic transition probabilities from the constants of the absorption formula.

THE experimental determination of the coefficient of absorption in the line spectrum of gases is beginning to be important, on account of the connection between the strength of absorption lines and the probabilities of transition between energy levels. The present paper contains discussions of the various steps encountered in translating the experimental data into atomic constants, and gives the necessary formulas, in form adapted for practical use. It was formulated at the suggestion of Dr. G. R. Harrison, who has recently made measurements of absorption coefficients in the principal series of sodium and potassium,[1] and who thought that a brief résumé of practical methods for reducing the data of such experiments might be of interest to other experimenters in the same field. I am indebted to Dr. Harrison for many valuable suggestions in writing the paper.

1. EXPONENTIAL LAW OF ABSORPTION

The product of experiment may be taken to be two spectrophotometric curves. The first shows the intensity of light at each point of the spectrum which has passed through the absorbing substance and reached the measuring device, whether this be photographic plate or other arrangement. The second similarly shows the intensity for the light which was received when the absorbing substance had been removed. The methods by which intensity of light is deduced from the observed photo-

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[1] G. R. Harrison, preceding paper in this issue.

graphic density need not be discussed here. These spectrophotometric curves will not truly represent the intensity distribution in the light which enters the spectrometer, on account of the finite resolution of the instrument, arising principally from the finite slit width, and the first step is to correct for this as far as possible. This correction is discussed in section 2.

The desired result is the absorption coefficient for each wave-length; that is, the relative decrease in the intensity of monochromatic light of that wave-length, passing through an infinitely thin sheet of the absorbing material, divided by the thickness of the sheet. The absorption coefficient can be deduced immediately when the true intensities of absorbed and non-absorbed light are known, provided we know also the distance x which the light has traveled in the absorbing material. For if I_0 represents the intensity of the light before absorption, I the intensity after traveling a distance x, and $k(\lambda)$ the absorption coefficient for wave-length λ, then by definition

$$dI/Idx = -k(\lambda) \tag{1}$$

from which immediately follows

$$I = I_0 \exp\left\{-k(\lambda)x\right\}, \tag{2}$$

where exp $\{\quad\}$ represents e raised to the power; and

$$k(\lambda)x = -\log(I/I_0) = \log(I_0/I). \tag{3}$$

2. Correction for Finite Resolution

In consequence of finite resolving power, the intensity distribution in the light which strikes the spectrometer is not truly represented by the resulting spectrum. If exactly monochromatic light should fall on the slit, a broadened band would result, on account both of the width of the slit and the finite resolving power of the optical system. As an approximation, we may suppose that this band has a sharply defined breadth Δ in units of wave-length on the spectrum, and that the illumination is constant over the band. Δ in general varies with the wave-length, and is assumed known. If the incident light is of continuous spectral distribution, it may be considered made up of a great many monochromatic components, extremely near to each other. Each such component produces a band of width Δ in the observed spectrum, the intensity in this band being proportional to the intensity of the monochromatic component in the actual spectrum. At a given point of the observed spectrum, there will be an overlapping of the bands from all actual wave-lengths within a range of $\Delta/2$ on either side of the actual wave-length associated with the point of the spectrum in question. Thus the intensity of the observed spectrum at a point of wave-length λ is the average, from $\lambda-\Delta/2$ to $\lambda+\Delta/2$, of the actual intensity. We are given these averages, and required to find the original curve.

If the true spectrum has an intensity which varies greatly in the spectral region Δ, the problem cannot be solved. This is the case where the instrument has not sufficient resolving power to resolve all the structure of the spectrum, and the structure cannot be deduced from the observations. On the other hand, if the spectroscope is of sufficient resolution for the spectrum which is being observed, it is easy to set up approximate methods of solving for the true spectrum. It should be noticed, however, that it is not in general possible to tell by examination of the observed spectrum whether there is unresolved detail or not; only our general knowledge of the nature of the spectrum in question can tell this.

In case we can be sure that the true intensity varies so little in a region of the order of Δ that we can express it by a power series of a few terms, we can find the true curve from the observed one by a method given by Runge.[2] Since this method does not seem to be well known, we give here the first approximation to it, obtained by supposing that the true intensity curve can be approximated by a parabola in a region of the order of Δ. Let the true intensity be $f(\lambda)$, the observed intensity $\varphi(\lambda)$. Then we approximate $f(\lambda)$ at $\lambda=\lambda_0$ by a parabola passing through the points $f(\lambda_0)$, $f(\lambda_0-\Delta/2)$, $f(\lambda_0+\Delta/2)$. This curve we may call $f_0(\lambda)$; its equation is

$$\begin{aligned} f_0(\lambda) &= f(\lambda_0)+[f(\lambda_0+\Delta/2)-f(\lambda_0-\Delta/2)]\,(\lambda-\lambda_0)/\Delta+ \\ &\quad 2\,[f(\lambda_0+\Delta/2)+f(\lambda_0-\Delta/2)-2f(\lambda_0)]\,(\lambda-\lambda_0)^2/\Delta^2\,, \end{aligned} \tag{4}$$

as may be seen by substitution. Then $\varphi(\lambda_0)$ is the average of $f(\lambda)$ from $\lambda_0-\Delta/2$ to $\lambda_0+\Delta/2$; and we may approximate by substituting $f_0(\lambda)$ for $f(\lambda)$.

$$\varphi(\lambda_0)=\frac{1}{\Delta}\int_{\lambda_0-\Delta/2}^{\lambda_0+\Delta/2} f_0(\lambda)d\lambda = f(\lambda_0)+[f(\lambda_0+\Delta/2)+f(\lambda_0-\Delta/2)-2f(\lambda_0)]/6 \tag{5}$$

To the approximation with which $f(\lambda)$ can be replaced by a parabola, the quantity

$$f(\lambda_0+\Delta/2)+f(\lambda_0-\Delta/2)-2f(\lambda_0)\,, \tag{6}$$

which is the only variable part of the coefficient of the square term in (4), must be independent of λ_0; for the coefficient of the square term of a parabola is independent of the choice of origin of coordinates. Then if (5) is regarded as defining $\varphi(\lambda_0)$ as a function of λ_0, φ equals $f(\lambda_0)$ plus a

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[2] See Paschen, Ann. der Phys. **60**, 712 (1897)

quantity relatively independent of λ_0; that is, φ is f slightly shifted bodily upward by an amount one sixth of (6). From the resulting similarity of the curves for φ and f, we may then replace (6) by

$$\varphi(\lambda_0+\Delta/2)+\varphi(\lambda_0-\Delta/2)-2\varphi(\lambda_0)\ , \tag{7}$$

so that (5) becomes

$$f(\lambda_0)=\varphi(\lambda_0)-[\varphi(\lambda_0+\Delta/2)+\varphi(\lambda_0-\Delta/2)-2\varphi(\lambda_0)]/6\ . \tag{8}$$

This suggests a simple construction for $f(\lambda_0)$, when φ is given: Connect the points $\varphi(\lambda_0+\Delta/2)$ and $\varphi(\lambda_0-\Delta/2)$ by a straight line. The line $\lambda=\lambda_0$ will then pass through $\varphi(\lambda_0)$ and through the mid point of the straight line. The intercept of $\lambda=\lambda_0$ between the straight line and the φ curve equals one half of (7), so that one third of the intercept is the constant in (8), to be subtracted from the φ curve to find the f curve.

3. CONSTANTS IN LINE ABSORPTION FORMULA

The formula of dispersion theory for the absorption coefficient may be written, if we are interested only in wave-lengths λ which are near enough the natural wave-length λ_0 so that $\lambda-\lambda_0$ can be neglected in comparison with λ_0,

$$k(\lambda)=\text{constant}/[(\lambda-\lambda_0)^2+\text{constant}']\ .$$

The two constants in combination determine the integrated absorption, while the second alone regulates the breadth of the line. For practical purposes, a convenient form for the constants proves to be that given by the equation

$$k(\lambda)x=C_1\log_e 10/[(\lambda-\lambda_0)^2+C_1C_2]\ , \tag{9}$$

where x is the length of path, as in (2) and (3), and the quantity $\log_e 10$ is inserted so as to bring the final formula in terms of logarithms to base 10, for convenience in computation. Then we can immediately write, from (3),

$$C_1/[(\lambda-\lambda_0)^2+C_1C_2]=\log_{10}(I_0/I)\ ,$$
$$(\lambda-\lambda_0)^2=C_1[1/\log_{10}(I_0/I)-C_2]\ . \tag{10}$$

Thus, if $(\lambda-\lambda_0)^2$ is plotted against $1/\log_{10}(I_0/I)$, a straight line should result, if the absorption coefficient really follows the formula of dispersion theory. This straight line has a slope C_1, and intersects the axis of abscissas at a point whose coordinate is C_2. The two constants can be read off at once from such a curve, simply by drawing the best straight line through the observed points, and finding its slope and intercept.

A case more likely to arise in practice is that in which the absorption coefficient is the sum of a term like (9), and a term which is approximately constant over the line. The latter can arise from continuous absorption, band absorption which does not vary greatly with wave-length, or small absorption on account of partial overlapping of neighboring lines. If we let $K(\lambda)$ be the total absorption coefficient, which should occur in (3), $k(\lambda)$ the part of it due to line absorption, given by (9), and k' the constant part, then $K(\lambda)=k(\lambda)+k'$. Instead of (10), we have

$$(\lambda-\lambda_0)^2=C_1\left[\frac{1}{\log_{10}(I_0/I)-k'x/\log_e 10}-C_2\right]. \tag{11}$$

When $(\lambda-\lambda_0)^2$ is plotted against $1/[\log_{10}(I_0/I)]$, this equation is easily seen to give, not a straight line, but a hyperbola. The most feasible way of solving for the constants of this equation seems to be to find by trial the value of $k'x$ such that when $(\lambda-\lambda_0)^2$ is plotted against $1/[\log_{10}(I_0/I)-k'x/\log_e 10]$, the result is a straight line, and then read off C_1 and C_2 as before. This amounts to finding by trial a fictitious value of I_0 equal to the actual I_0 multiplied by exp $\{-k'x\}$, or the intensity which the incident beam would have if subjected to the continuous absorption but not to the line absorption, and treating this as the incident intensity for line absorption. The same method can be used if the true incident intensity I_0 is not well known, the intensity being simply adjusted by trial until the resulting curve is a straight line. It is found in practice that the constant $k'x$ can be readily determined by a small number of trials. This method not only serves to determine the constants of line absorption when continuous absorption is also present, but it also furnishes a rather sensitive determination of the amount of continuous absorption, separating it satisfactorily from the line absorption.

4. Possible Errors in the Case of very Narrow Absorption Lines

Experimenters are inclined to specify a line by its half breadth and area, or by some such method, and this will be discussed in the present section. Errors are likely to appear when lines are described in this manner, because the shape of a line varies as we pass through the absorbing medium. Suppose we have a substance with a narrow absorption line, and pass white light through a moderate length of it. If we have the proper length column, almost all the light will be removed in the wave-lengths in the center of the line, while considerable light will get through of the wave-lengths at the edge of the line. But suppose now the length of column is greatly increased. Very little more light from the center of the line will be absorbed, simply because there is very little left to be absorbed; but light from the edges, where the absorption coefficient is much less than in the center, but still appreciable, will be absorbed, so that light from a wider band of wave-lengths will be removed from the spectrum. As the length of the absorbing column becomes greater and greater, light is removed from a broader and broader region, until finally, if a long enough column could be used, the light from the whole spectrum would be absorbed. Under these circumstances, it is plainly of no direct significance to speak of the half breadth in the spectrum of the transmitted light.

Analytically, we can easily see the same thing. If the absorption coefficient has the value given in (9), then from (2) we have

$$I=I_0\exp\{-C_1\log_e 10/[(\lambda-\lambda_0)^2+C_1C_2]\}\ , \tag{12}$$

where as before exp denotes the exponential. For small values of C_1 (it will be remembered that C_1 contains x, the thickness of the medium, as one of its factors), this can be approximated by

$$I=I_0\{1-C_1\log_e 10/[(\lambda-\lambda_0))^2+C_1C_2]\}\ . \tag{13}$$

If here C_1 were to change, that would not change the shape of the absorption line, which can best be defined by $(I_0-I)/I_0$. But when the exponential can no longer be replaced by its first two terms, $(I_0-I)/I_0$ no longer remains of the same shape.

In the region where (13) holds, the half breadth is the distance between the two points where $(I_0-I)/I_0$ has half its maximum value. It is immediately seen to be

$$2\sqrt{C_1C_2} \tag{14}$$

in wave-length measure. In this same region, the area under the curve $(I_0-I)/I_0$, integrated over all wave-lengths, is

$$\pi\log_e 10\sqrt{(C_1/C_2)}\ \cdot \tag{15}$$

Closely connected with the change in shape of a line, described above, is the fact that the exponential law (2) does not hold if the observed, rather than the true, intensities are used. For suppose an extreme case, in which the slit was so broad that monochromatic light would be spread out into a broad band compared with the natural breadth of the line we are interested in. Then, from the formulas in sections 2 and 4, we should have the observed intensity equal to $I_0\int d\lambda\ \exp\{-k(\lambda)x\}$, the integral being over the band of width Δ, within which $k(\lambda)$ varies greatly. This does not by any means vary with x as an exponential function, so that the method of section 1 cannot be used to determine the absorption coefficient. In this case, which is essentially the situation where the resolution of the instrument is insufficient to resolve the detail, there seems to be no direct way of finding the absorption coefficient from the data. When the resolution is sufficient, the only correct method seems to be to apply the slit width correction, obtain the absorption coefficient from the exponential law, (2) or (3), and work with this coefficient. This seems not to be generally appreciated by experimenters.

5. CONSTANTS IN THE QUANTUM THEORY OF ABSORPTION

A quantum theory of dispersion and absorption has recently been proposed by the author,[3] leading to an absorption formula of the type (9). The connection between the constants C_1 and C_2 and the theoretical constants will now be derived. The derivation could be made, as usual in dispersion theory, by considering the amplitudes and phases of the wavelets emitted by the atoms under the action of radiation; but the same result can be more easily obtained by direct use of the energy principle. It was assumed in that paper that if light whose energy density in frequencies between ν and $\nu+d\nu$ was $\rho(\nu)d\nu$, shines on atoms in the ith stationary state, then there was a probability $B(\nu)\rho(\nu)d\nu$ that each atom would, in unit time, have a transition to the jth state, with increase of energy $h\nu_0$, where ν_0 is the frequency of the transition i-j. $B(\nu)$ is a function of ν, characteristic of the transition i-j, and its value will be given in (17). The energy going into the increased atomic energy was further shown to be abstracted, on the average, from the radiation of frequency ν passing over the atoms. If then there are N atoms per unit volume in the ith state, there are Ndx in a sheet of unit cross section and height dx; and if light of density as specified above shines along the x axis, energy $Ndx\ B(\nu)\rho(\nu)h\nu_0 d\nu$ per second will be abstracted from the light and communicated to the atoms. An amount of energy $c\rho(\nu)d\nu$, where c is the velocity of light, flows through the sheet in a second. Thus the fraction of the energy of the light which is removed by passing through the sheet is $Ndx\ B(\nu)h\nu_0/c$. This is the same as the fractional decrease in intensity, so that we have by (1)

$$-dI/Idx = k(\lambda) = NB(\nu)h\nu_0/c. \tag{16}$$

It is further assumed in the paper quoted that

$$B(\nu) = B_{ij}\frac{(1/\pi)\ (P_i+P_j)/2\pi}{[\nu-\nu_0]^2+[(P_i+P_j)/2\pi]^2}, \tag{17}$$

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[3] J. C. Slater, Phys. Rev. **25**, 395 (1925)

where B_{ij} is the same as Einstein's coefficient of probability B, and P_i and P_j are respectively the probabilities of leaving the states i and j. The quantity P_i+P_j determines the broadening; and since there is no need for the present purpose to confine ourselves to the specific theory of broadening involved in this formula, we shall write P in place of P_i+P_j, and make no explicit connection between P and other quantities. We then have

$$k(\lambda)x=\frac{NB_{ij}xh\nu_0}{\pi c}\frac{P}{2\pi}\frac{1}{[\nu-\nu_0]^2+[P/2\pi]^2}\,. \tag{18}$$

To compare this with (9), we substitute for λ in terms of ν. We shall suppose λ to be measured in angstrom units. Then $\nu=c/(\lambda\times10^{-8})$. Treating $(\nu-\nu_0)$ as a small quantity, which is allowable with the approximations we are making, $\nu-\nu_0=-10^8c(\lambda-\lambda_0)/\lambda_0^2$. Then (18) becomes

$$k(\lambda)x=\frac{NB_{ij}xhP\lambda_0^3}{2\pi^2c^2\,10^8}\frac{1}{[\lambda-\lambda_0]^2+[P\lambda_0^2/2\pi c10^8]^2}\,. \tag{19}$$

By comparison, we see that this is of the same form as (9), and that the constants are given by

$$C_1=NB_{ij}xhP\lambda_0^3/2\pi^2c^210^8\log_e10;\ C_1C_2=[P\lambda_0^2/2\pi10^8c]^2. \tag{20}$$

From these we solve for the two constants B_{ij} and $P/2\pi$ determining the total absorption and breadth of the line

$$B_{ij}=\frac{\pi c\log_e10}{Nxh\lambda_0}\sqrt{\frac{C_1}{C_2}}\,;\quad \frac{P}{2\pi}=\frac{10^8c}{\lambda_0^2}\sqrt{C_1C_2}\,. \tag{21}$$

Finally, we may determine Einstein's probability A_{ij} from this by the equation $A_{ij}=(8\pi h\nu_0^3/c^3)B_{ij}$, disregarding the effect of a priori probabilities. Then

$$A_{ij}=\frac{8\pi^2c\log_e10\times10^{24}}{Nx\lambda_0^4}\sqrt{\frac{C_1}{C_2}}\,. \tag{22}$$

It is to be recalled that in Eqs. (19) to (22), λ_0 is to be expressed in angstrom units.

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