AN APPROXIMATION METHOD AND APPLICATION TO SOME HCl BANDS

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Abstract

A method of approximation applicable to some experimental investigations is based on the inversion for $\mu(\nu)$ of the integral equation

$$A(x)=\int_0^\infty (1-e^{-\mu(\nu)x})d\nu$$

The general nature of the interdependence of $A(x)$ and $\mu(\nu)$ is described and a practicable method of characterizing certain types of $\mu(\nu)$ is developed in sufficient detail to permit of immediate application of the results. The author's previously published data for the HCl fundamental band lines has been approximated by line patterns based on the hypothesis of (a) a Doppler broadening or error curve structure, (b) a Stark broadening due to the molecular force field set up by neighboring molecules, and (c) an interrupted absorption process or dispersion curve type. The modifications attendant on recognizing the isotopic doubling of the lines are predictable from the calculation for a doublet structure of infinite component separation. The values of the line intensities and breadths and the Einstein coefficients A_{01} and B_{01} are given for each of the assumed structures. Kinetic theory considerations make it improbable that the Doppler effect is the primary determining influence as regards line shape. The Lorentz line with a possible Doppler broadening superposed would seem to reproduce the experimental data satisfactorily. The results are in keeping with an atomic binding for HCl and if the atomic character of the dissociation products be accepted it appears that the dielectric constant measurements lead indirectly to the order of magnitude of our values for $\int_0^\infty \mu(\nu)d\nu$. This lends further support to Van Vleck's criticism of that explanation of the discrepancy between the extrapolated optical and direct measurements of the dielectric constant of HCl which depends on an appeal to the infra-red vibration bands. Some aspects of the recent work on the coupling effect in gases are examined and Badger's data in the pure rotational spectrum of HCl have been studied on the assumption of a line structure derived on the basis of such "coupling" pressure broadening. The value for the line intensity found here is in slightly better agreement with the new quantum theory but the discrepancy is still excessive.

A PREVIOUS communication[1] on the results of an investigation of the HCl fundamental infra-red vibration-rotation band concerned itself primarily with the relative strengths of the band-lines for the determination of which it was not crucial to know very precisely their structure and nature, although these matters were considered at some length. It is proposed in this paper, among other things,[2] to amplify our earlier discussion of the experimental area versus tube-length curves and to take up more critically the form and breadth of the lines and their absolute intensities. Recent developments in the quantum theory have stressed the quantitative prediction of line intensities and their correlation with other experimentally

[1] D. G. Bourgin, Phys. Rev. **29**, 794, 1927. This paper will be referred to as I.

[2] D. G. Bourgin, Phys. Rev., **31**, 704 1928,

determinable magnitudes. Such information as this paper affords in the way of experimental estimates of absolute intensities is therefore expected to be of immediate application. Certain other extensions and applications of experiment will also be touched on in the course of this work.

The method of approximation developed here for the analysis of the curves of line-area versus tube-length is applicable to all similar spectroscopic investigations (*cf* for instance the application to Badger's infra-red data) in which the resolution is insufficient to permit the use of Beer's law, as well as to data obtained in other fields.

Briefly our problem may be stated as follows: $A(x)$ is supposed known for real positive x and is defined by

$$A(x)=\int_0^\infty (1-e^{-\mu(\nu)x})d\nu \tag{1}$$

We wish to determine $\mu(\nu)$ or less ambitiously to characterize it as regards certain properties. To fix our attention we may interpret $A(x)$ as the total light absorption due to the interposition of a medium of absorption coefficient $\mu(\nu)$ and thickness x between light source and receiver. If we are dealing with an absorption line we should be interested in its height $(\mu(\nu)_{\text{maximum}})$, its width defined for a singlet line as its breadth in frequency units measured for the ordinate $\mu(\nu)_{\max}/2$, and its intensity $(\int_0^\infty \mu(\nu)d\nu$ or the equivalent quantity $dA(0)/dx)$.

Some aspects of the problem have been investigated in a mathematical paper. We shall restate some of the results of that paper[3] and first we remark that if $\mu(\nu)$ satisfies certain restrictions it is possible to derive an explicit formula for $\mu(\nu)$ in terms of known functions and their integrals. This solution will not be used here, however, because of practical difficulties of application. Instead we shall discuss the implications of some qualitative theorems correlating the variation in form of $\mu(\nu)$ with the properties of $A(x)$. The practicable determination of the characteristics of $\mu(\nu)$ proceeds thus: we assume (on the basis of theory or otherwise) a certain functional form for $\mu(\nu)$ involving arbitrary parameters. The parameters are determined by comparison of $E(x)$ and $A(x)$ where the notation refers to the experimental and computed ordinates (from (1)) respectively.

Consider integrable even functions $\mu(\nu)$ which are continuous and monotone decreasing on the interval $(0,\infty)$. It is then true[3] that if the curve* $\mu_1(\nu)$ vs ν and the curve $\mu_2(\nu)$ vs ν intersect just once in the interval $(0,\infty)$ and $\mu_1(\nu)\geqq\mu_2(\nu)$ on the interval up to the point of intersection and $\mu_2(\nu)\geqq\mu_1(\nu)$ for the remainder of the interval and if $\int_0^\infty\mu_1(\nu)=\int_0^\infty\mu_2(\nu)d\nu$ then $A_2(x)>A_1(x)$, $dA_2(x)/dx>dA_1(x)/dx$ for sufficiently small positive x, and $dA_2(x)/dx<dA_1(x)/dx$ for sufficiently large x. The important characteristic of the $A_2(x)$ curve is that it has a more pronounced "bend" than the $A_1(x)$ curve, and this observation suggests the direction in which to modify a preliminary

[3] We shall refer to this paper as II. It will appear shortly in the Tokohu Mathematical Journal.

* It is suggested that the reader draw graphs to illustrate these theorems.

choice for $\mu(\nu)$ in order to attain a closer representation of a given curve. For the case of doublet lines, somewhat similar theorems are true.

The fundamental conditions on the computed functions will now be developed. Unless otherwise stated we shall materially simplify our exposition by insisting that $\mu(\nu)$ involve two parameters only and furthermore we impose the separability condition, namely, that there exists a transformation defined by

$$z=(\nu-\nu_0)f(\alpha,\beta) \tag{1.1}$$

such that

$$\begin{aligned}\mu(\nu)&\equiv\mu(\nu-\nu_0,\alpha,\beta)\\&=F(\alpha,\beta)\phi(z)\end{aligned} \tag{1.2}$$

where the notation indicates that α and β do not occur explicitly in $\phi(z)$.

Our approximation method assumes

$$E(x)=[1/f(\alpha,\beta)]\int_{-\nu_0}^{\infty}(1-e^{-F(\alpha,\beta)x\phi(z)})dz \tag{1.3}$$

The lower limit may generally be replaced by $-\infty$ and on introducing n to designate the product $xF(\alpha,\beta)$ we obtain

$$E(x)f(\alpha,\beta)=\int_{-\infty}^{\infty}(1-e^{-n\phi(z)})dz=A(n) \tag{1.4}$$

Clearly the evaluation of $A(n)$ does not involve knowledge of the parameters. It is evident from Eq. (1.4) that the curve for $E(x)$ vs. x is derivable from the curve for $A(n)$ vs. n by appropriate linear modification in the scale of n and $A(n)$ (i.e., an affine transformation). We now indicate two methods of testing the adequacy of an assumed $\mu(\nu)$.

Suppose, that $\mu_1(\nu)$ leads to a perfect representation of the $E(x)$ vs. x curve in the sense that the computed $A(n)$ vs. n curve is transformable into the $E(x)$ vs. x curve by an affine transformation. We must have

$$E(x_1)/A(n_1)=E(x_2)/A(n_2) \tag{2}$$

subject to the condition $x_1/n_1=x_2/n_2=\lambda$. Writing $x_2=x_1+\Delta x$ and $n_2=n_1+\Delta n$ and noting that $\Delta x/\Delta n=\lambda$ we infer

$$\frac{A(n+\Delta n)-A(n)}{A(n)\Delta n}=\frac{E(x+\Delta x)-E(x)}{\lambda E(x)\Delta x} \tag{2.1}$$

$$\frac{A(n)x(dE(x)/dx)}{E(x)n(dA(n)/dn)}=1 \tag{2.11}$$

This may also be written

$$\frac{d\log E(x)}{d\log x}-\frac{d\log A(n)}{d\log n}=0 \tag{2.12}$$

The relation 2.12 (or 2.11) is fundamental to the theory and because of its independence of scale factors indicates immediately whether or not a given type of $\mu(\nu)$ is adequate. One plots $d \log E(x)/d \log x$ vs. x and $d \log A(n)/d \log n$ vs. n on the same graph paper—for perfect representation the graphs should coincide throughout. An alternative method of testing an assumed form of $\mu(\nu)$ is to determine the transformation $n=\lambda x$, $Y=A(n)/\rho$ required to make the curve $y=Y(x)$ coincide with the experimental curve $y=E(x)$ at two arbitrary points x_1 and x_2 and then to compare the corresponding complete curves. To fix λ we have only to solve graphically the equation

$$A(\lambda x_1)/A(\lambda x_2)=E(x_1)/E(x_2)$$

Then ρ is determined by

$$A(\lambda x_1)/\rho \equiv Y(x_1)=E(x_1)$$

If the curve $y=Y(x)$ agrees with the curve $y=E(x)$ within the limits of experimental error throughout the range of observation, we may compute the corresponding integral absorption coefficient α from

$$\alpha \equiv \int_0^\infty \mu(\nu)d\nu=(dY/dx)_{x=0}=(1/\rho\lambda)(dA/dn)_{n=0} \tag{2.4}$$

The uncertainty in the determination of α will evidently be compounded of the uncertainty regarding the correct form of $\mu(\nu)$ and the uncertainty in the determination of $\rho\lambda$. In the absence of a rigorous theory of line

TABLE I. *Tabulated values of the fundamental approximating functions.*

n	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$	n	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$
.1		0.1562	0.1532	1.	0.6415	1.494	1.26
.2		0.315	0.2984	2.	0.9812	2.845	2.09
.3				3.	1.1692	4.0527	
.4				4.	1.3175		
.5	0.378	0.807	0.699	5.	1.4115	6.2	3.69
.6				6.			
.7				7.			
.8				8.			
.9				9.			
				10.		9.127	52.7
				50.			12.4

broadening free from arbitrary assumptions, we can only estimate the uncertainty in α due to uncertainty regarding the form of $\mu(\nu)$ by trying several different forms for the function $\mu(\nu)$ and observing the variation in α for those forms which fit the empirical data adequately. The fractional uncertainty in α due to uncertainty in the determination of $\rho\lambda$ is easily calculated from the uncertainties M_1 and M_2 in the values of the experimental absorption $E(x_1)$ and $E(x_2)$. It has the value

$$\left|\frac{\delta\alpha}{\alpha}\right| = \left| \begin{vmatrix} M_2 \end{vmatrix} \quad \begin{vmatrix} [n_1A'(n_1)-A(n_1)] \end{vmatrix} \right| \div \rho \begin{vmatrix} A(n_2) & n_2A'(n_2) \\ A(n_1) & n_1A'(n_1) \end{vmatrix}$$

where $n_1=\lambda x_1$; $n_2=\lambda x_2$; $A'(n_1)=(dA/dn)_{n=n_1}$; $A'(n_2)=(dA/dn)_{n=n_2}$.

This, of course, is an upper limit to the uncertainty in α since in practice the curve $y=A(\lambda x)/\rho$ must fit the experimental curve within its limits of error not only at the points x_1 and x_2, but throughout the range of observation. The application of Eq. (2.5) to the computations of the HCl fundamental band is given on page 246.

We shall now systematically investigate some rather important forms for $\mu(\nu)$. The first function to be considered is that giving the line-shape of an originally infinitesimally thick line on the assumption of a Doppler broadening.

$$\mu_D(\nu) = Pe^{-c(\nu-\nu_0)} \tag{3}$$

(From another point of view this is merely the error curve in ν units.) Since ν_0 is generally very large we may write the total absorption in the form

$$A(x) = \int_0^\infty \{1-\exp\,[-xPe^{-c(\nu-\nu_0)^2}]\} \tag{3.1}$$

A simple transformation allows us to write

$$A(x) = (2/c^{1/2}) \int_0^\infty \{1-\exp[-ne^{-z^2}]\}\,dz = (2/c^{1/2})\psi_D(n) \tag{3.2}$$

where $n=Px$. $\psi_D(n)$ is calculated in Table I for sufficient values of n to make an accurate graph possible. For large n values a method of graphical integration[5] was used. For small values of n the results were checked by evaluation of the series

$$\psi_D(n) = (\pi^{1/2}/2)\sum(-1)^{N-1}n^N/N!N^{1/2} \tag{3.3}$$

or

$$\psi_D(n) = 0.8862\{n-0.35355n^2+0.096225n^3-.02083n^4+.00285n^5\} \tag{3.31}$$

The peak height, breadth and intensity for this line structure are respectively P, $(\log 4/c)^{1/2}$, $P\ (\pi/c)^{1/2}$.

It will be noticed that the line intensity may be expressed as $cnA(x)/x\psi(n)$. We shall refer to this result as Theorem A and it may be shown without difficulty that this is always the case provided $\mu(\nu)$ involves the parameters α and β separably even if $\mu(\nu)$ contains x provided* only that $(\partial/\partial x)\int_0^\infty \mu(\nu)d\nu = 0$. In this latter case, however, although the ratio $A(x)/\psi(n)$ occurs, the approximating function is not $\psi(n)$ but $\psi(n)/f(\alpha,\beta,\lambda(n,\alpha,\beta))$ where $f(\alpha,\beta,x)$ is

[5] $\psi_D(n)$ was written as $\int_0^1(1-\exp[-ne^{-z^2}])dz+\int_0^1(1-\exp[-ne^{-1/z^2}]dz/z^2$ and the area under the integral curves was obtained by counting squares.

* This is the case, for instance, for pressure broadening (see p. 243).

the analogue of $f(\alpha,\beta)$ Eq. (1.1) and $\lambda(n,\alpha,\beta)$ is the value of x expressed in terms of n, α and β.

The next line-shape to be taken up is that suggested by a consideration of a Stark broadening[6] of an absorption line induced by the presence of neighboring molecules. On using Holtsmark's expression[7] for the probability that a given field exist at a point and the assumption of a uniform shift dependent on the square of the molecular field, the author has derived

$$\mu(\nu) = k(\nu/c)^{1/2}/c(1+\nu/c)^2 \tag{4}$$

$$A(x) = c\int_0^\infty (1-e^{-nz^{1/2}/(1+z)^2})dz = c\psi_S(n)$$

where $n = kx/2c$. The values of $\psi_S(n)$ given in Table I were evaluated for small n from the series

$$\psi_S(n) = 2n\left[\frac{\pi}{4} - \frac{n}{2!}\frac{1}{12} + \frac{n^2}{256}\frac{\pi}{4} - \frac{n^3}{3!}\frac{1}{210} - \frac{55\pi n^4}{(65536)^2}\right] \tag{4.1}$$

$$= 1.5708n - 0.0825n^2 + 0.0061359n^3 - 0.000397n^4 - 0.00002197n^5 \tag{4.11}$$

These values are closely the same as those determined by a graphical integration[8] by means of which the tabulation was extended to higher n values.

Peak absorption takes place for $\nu = c/3$. The width is obtained by solving for the difference of the two positive roots of $\mu(\nu)_{max}/2 = (k/4c)(\nu/c)^{1/2}/(1+\nu/c)^2$. This turns out to be 1.8937 c. The asymmetry of the curve is so pronounced that the width affords only slight information about the true curve form. The integrated absorption coefficient is $n\pi A(x)/2x\psi_S(n)$ or $\pi kc/4$.

For completeness[1] the results for the line-shape predicted by theories depending on finite wave train emission (or absorption), for instance, the collision interruption of emission as postulated by Lorentz, are also given. Here

$$\mu(\nu) = a/[(\nu-\nu_0)^2+b^2] \tag{5}$$

We readily derive

$$A(x) = 2b\psi_L(n) \tag{5.1}$$

where

$$\psi_L(n) = \pi\left\{\frac{n}{2} - \frac{2n^2}{8} + \frac{n^3}{32} - \frac{5n^4}{768} + \frac{7n^5}{6144} - \cdots\right\} \tag{5.2}$$

[6] The derivation is somewhat long and is omitted, inasmuch as the type of curve does not fit the HCl data. Professor E. C. Kemble has remarked to the writer that the inadequacy of the Stark effect curves is evident *a priori* from the fact that the HCl lines show no pressure shift.

[7] J. Holtsmark, Ann. d. Physik, **58**, p. 677 (1919).

[8] The graphical integration depends on the representation of $\psi(n_S)$ in the form

$$2\int_0^1 (1-e^{-nz^{1/2}/(1-z)^2})dz + 4\int_0^1 (1-e^{-nz_1^3/(1+z_1^2)^2})dz_1/z_1^2.$$

In some investigations the data correspond to increase of pressure rather than gas-column length. Admixture of foreign gases is found to be far less effective in modifying line-shape than addition of the absorbing gas. Formally, this may be taken account of on the Lorentz theory by presupposing a large difference in the diameter of a molecule depending on whether its neighbors are of the same or different types; however it seems desirable to consider theories which connect up more intimately the nature of the added gas and the resultant change in line-shape. The application in this paper will be to Badger's ultra-red work. In order to establish plausible formulae we advert to some work on atomic spectra. Two recent papers have taken up the problem of the coupling, or resonance effect, of atoms in similar quantum states, under the idealization of no temperature agitation. Mensing,[9] using quantum-theoretic ideas, has derived the perturbation function on the assumption that only two molecules are involved, while Holtsmark[10] considers a set of classical oscillators vibrating parallel to the electric vector of the incident wave and determines the set of fundamental frequencies of this system. Mensing derives a line-breadth dependent on N (the number of atoms, or molecules, per cc) while Holtsmark finds that the variation is proportional to $N^{1/2}$. (Schuetz[11] confirms Holtsmark's line-breadth variation in the case of Na absorption, but in view of the extreme simplications introduced it is hardly likely that either treatment is quantitatively correct.)

It has been urged by commentators as a basic objection, that the time of passage of one atom through the sphere of action of another is of the order of 10^{-12} seconds, which is infinitesimal in comparison with the usual mean life of 10^{-8} seconds and hence that the resonance effect is insignificant. It seems plausible, however, that the criterion to be applied is rather that of the number of periods during which appreciable influence is exerted. For atomic frequencies this is of the order of 10^3 or greater, though for slow molecular rotation the value is very much less. For instance, the lower rotational states of HCl have a frequency of about 10^{12} so that there may be a real objection to extending the coupling concept to the ultra-red rotation bands.

As a possible refinement of the treatment (particularly Holtsmark's) it seems suggestive to approximate the effect of the short coupling interval by subjecting the neighboring atoms to arbitrary phase shifts with a random distribution in time and it is hoped to present results on this extension at some later time.

If an error-curve line-structure be assumed we expect

$$\mu_p(\nu) = Pe^{-\alpha(\Delta\nu)^2/p^s}/p^{(s-2)/2}$$

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

[10] T. Holtsmark, Zeits. f. Physik, **34,** p. 122 (1925).

[11] Schuetz, Zeits. f. Physik, **34,** p. 122 (1925). Schuetz objects to Holtsmark's results because of the Gaussian error curve form of absorption line. However, this line structure is not inherent in Holtsmark's derivation which merely leads to a mean square value of the frequency shift dependent on N.

where $s=1$ for Holtsmark's conclusion and 2 for that of Mensing. The form of $\mu_p(\nu)$ is easily checked when it is remembered that the intensity is a linear function of the number of mol./cc and hence of the pressure and that the mean square value of $\Delta\nu$ is to be proportional to N^s.

This $\mu(\nu)$ satisfies all the conditions of Theorem A and it is obvious that $\psi(n)$ is our previously tabulated $\psi_D(n)$. Therefore

$$\int_0^\infty \mu(\nu)d\nu = \pi n A(p)/2p\psi_D(n) \tag{6.1}$$

For $s=1$, $n=Pp^{3/2}$ and it is immediately corroborated that our approximating function is $n^{1/3}\psi_D(n)$ and that $A(p)=2n^{1/3}\psi_D(n)/P^{1/3}\alpha^{1/2}$.

The alternative assumption $s=2$ implies an approximation function of the form $n\psi_D(n)$. It may be remarked in passing that though Holtsmark's theory is not extensible[12] to a frequency distribution of the type $\mu_L(\nu)$, the interpretation[13] of the constants in the Lorentz theory yields the pressure broadening formula

$$\mu(\nu)=\frac{\alpha p^2}{(\nu-\nu_0)^2+\beta^2 p^2} \tag{7}$$

It does not seem possible to approximate doublet lines easily by the method of this paper. We may characterize the difficulty by the observation that the line shapes for different values of the separations of the components are not similar, or put otherwise that it is not possible to separate the parameters so as to permit of reducing all curves to the same normal form by an affine transformation.[14] The determination of the parameters by a method of successive approximation would in general be tedious. Reducible cases arise for very small or very large doublet separations. For the first circumstances we use the singlet structure; for the latter we write

$$\mu(\nu)=\mu_1(\nu-\nu_1)+\mu_2(\nu-\nu_2) \tag{8}$$

and since $\nu_2-\nu_1$ is assumed very large we have

$$A(x)=\int_0^\infty \left\{2-e^{-\mu_1(\nu)x}-e^{-\mu_2(\nu)x}\right\}d\nu \tag{8.1}$$

[12] Inasmuch as the mean square value of $\Delta\nu$ is infinite.

[13] Lorentz' derivation makes it clear that b(cf. Eq. 5) is linear in N and therefore p, and the condition that the intensity be linear in N determines the quadratic dependence of a on p.

[14] Consider for example the doublet line given by

$$\mu(\nu)=P\left\{\frac{k}{(\nu-\nu_1)^2+b^2}+\frac{1-k}{(\nu-\nu_2)^2+b^2}\right\}$$

where ν_1, ν_2 and k are usually known. We might reduce this to

$$\mu(\nu)=f(P,b)\left\{\frac{k}{z^2+1}+\frac{1-k}{[z-(\nu_2-\nu_1)/b]^2+1}\right\}$$

or some similar form but it is not possible to write this as $f(P, b)\,\phi(z)$.

Using the subscript T to indicate an infinitely separated doublet structure, there results

$$\psi_T(n)=\psi(kn)+\psi((1-k)n) \quad 0<k<1 \tag{8.11}$$

so that we may get the $\psi_T(n)$ functions directly for each of the line shapes from the tabulated singlet line functions of Table I.

Some of the special line structures taken up above will first be applied to the author's data on the fundamental band of HCl. Table II gives the numerical values deduced for each of the line types including the Lorentz collision broadened line for which the results have already been published.

TABLE II. *Comparative calculations for the HCl fundamental band.*

	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$	$\psi_{DT}(n)$	$\psi_{LT}(n)$
$\int_0^\infty \mu(\nu)d\nu$	40.06×10^{10}	33.7×10^{10}	45.5×10^{10}	40.9×10^{10}	37.7×10^{10}
Width	7.479×10^{10}	2.1×10^{11}	2.3×10^{10}		
Width each component					1.2×10^{10}
$dp(r_0)/dr$	0.89×10^{10}		0.888×10^{10}	0.84×10^{10}	0.836×10^{10}
A_{01}	38		40	38	39
B_{01}	84 $\times10^{14}$		96 $\times10^{14}$	85 $\times10^{14}$	84 $\times10^{14}$

In order to obtain an indication of the direction of modification required by a consideration of the isotope doubling, an approximation was made using the assumption of infinite component separation (i.e., $\psi_T(n)$) and the known isotope distribution, 77:23. The line intensities calculated for the error curve and the Lorentz line doublets are somewhat less than the value obtained for an assumed singlet structure. It seems plausible to expect that an approximation function, based on a finite doublet separation would yield constants intermediate between those calculated by means of the $\psi(n)$ and $\psi_T(n)$ curves.

Fig. 1 is indicative of the degree of accuracy with which the various line shapes are capable of representing the experimental data. The curves are the graphs of the functions $A(x)$ for the lines $M=2$, 3, 4 where the ordinate scales have been adjusted so that the various curves are superposed as nearly as possible (actually it is clear that a slight reduction in the ordinate scale for the lines $M=2, 4$ would bring the three curves in much closer coincidence). It is evident that there is but slight variation in the experimentally determined total absorption-curve shape. The attempt was made to approximate the line $M=3$ most closely. It will be observed that the deviation of the computed points is small and also that practically all the computed points are below the corresponding point on the experimental curve for short tube-lengths; hence it is possible that our estimates[15] for $\int_0^\infty \mu(\nu)d\nu$ may be somewhat low. The approximation by the Stark curve

[15] Slightly more accurate values for the points on the $\psi_L(n)$ curve account for the fact that this paper's estimate of $\int_0^\infty \mu_L(\nu)d\nu$ is somewhat lower than that given in I.

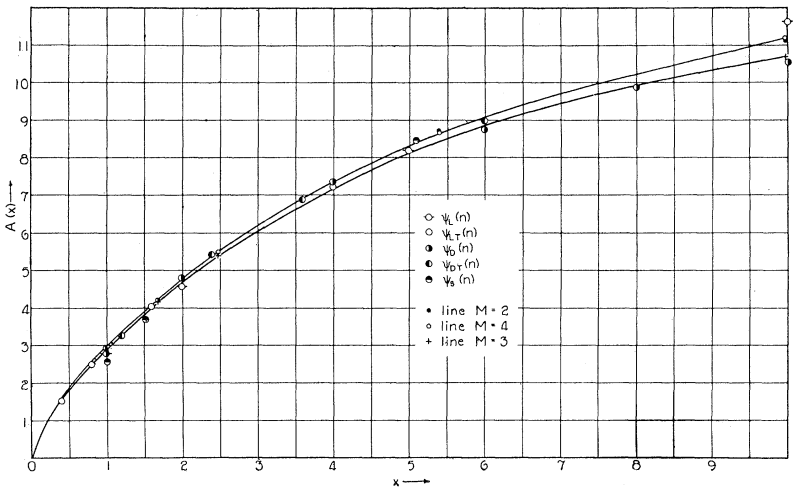

Fig. 1. Comparison of experimental and computed total absorption.

is decidedly forced and hence not plausible. There are objections to the Doppler structure. The theoretical expression for a Doppler line has often been derived on the basis of kinetic theory considerations in the form

$$\mu(\nu) = P(\lambda, T \cdots) e^{-m\lambda_0^2(\Delta\nu)^2/2kT} \tag{9}$$

The broadening given by Eq. (9) is about 1.76A as against the value 24.7A calculated from the fitting of the experimental curve by $\psi_D(n)$. Of course it is still possible that the true line shape has the characteristics of an error curve even though the Doppler explanation is invalid.

The Lorentz curve taking into account the doublet structure seems to provide a fairly faithful delineation of the absorption line. The breadths calculated for the components of the Lorentz line are of the order of 10^{10} frequency units which is about half that obtained on the assumption of a singlet line and only some three times the width expected theoretically on the basis of a Doppler widening (assuming the constants for the infinitely separated structure). The indications are, therefore, that a more refined test would favor the superposition of a Doppler broadening on a dispersion-curve pattern.

Two important questions, which can be answered only partially here are, (A) the variation possible in the integrated absorption coefficient computed from a given line pattern; (B) the range of variation of the estimates of the intensities as derived from various line shapes.

Eq. (2.5) assigns an upper bound to the differences contemplated in (A). A rough calculation based on an approximation by means of the $\psi_L(n)$ curve using the values $M=6$ for $x=1$ cm and $M=1$ for $x=0.1$ cm indicates a maximum inaccuracy of about 8 percent. As regards the possibility of widely divergent estimates of intensity for different line types, we may reason plausibly from the results tabulated in Table II. Of the five line

shapes investigated, the four that fit the observations adequately yield estimates whose maximum deviation from each other is about 20 percent and whose deviation from the mean value is about 10 percent. The values yielded by the Stark curve are useful as suggesting limiting values for the possible deviations since this curve is so decidedly inferior as to be really incompatible with the experimental evidence. Nevertheless, even here the intensity is only some 20 percent lower than the mean and 30 percent lower than the maximum recorded computed intensity.

Our expectation is, therefore, that the approximation method yields results correct within 20 percent. When allowance is made for unavoidable experimental error (cf. I) it appears that 30 percent is a fair estimate for the accuracy of the absolute intensities.

Dennison[16] has recently presented a carefully worked out theory of line broadening. Without prejudicing the merit of his independent derivation it may be pointed out that this theory may be shown to be closely akin to that of Lorentz and leads, in fact, to the same expression for the line structure, namely, $\mu_L(\nu)$ (cf Eq. (5))—moreover, except for a difference in the value of a numerical constant the theoretical interpretations of a and b are identical with those which may easily be derived from Lorentz's work, i.e.,

$$b = kN\sigma^2/(hm)^{1/2}\ ;\quad a = \int_0^\infty \mu(\nu)d\nu = b/\pi \tag{10}$$

where the usual kinetic theory notation has been adhered to and the constant k has the value $k_L \equiv (8/\pi)^{1/2}$ in Lorentz's work and $k_D \equiv (7/4\pi)^{1/2}$ in Dennison's.

It does not seem that Dennison noticed this close relationship between his results and those of Lorentz and that therefore his demonstration of the adequacy[17] of his expression for $\mu(\nu)$ to represent the author's data is already contained in the writer's use of $\mu_L(\nu)$ in I. A comparison of Dennison's values for the total absorption as computed from Paton's data on a 4 cm tube shows that they are in excellent agreement with the writer's absorptions for short tubes (except possibly with the least reliable of the writer's measurements, namely, those for the 2.97 cm tube).

The knowledge of b or a enables us to estimate the effective molecular diameter σ and it is clear that the ratio of the Lorentz to the Dennison value will be $(k_D/k_L)^{1/2} = 2+$. This expectation is, in fact, substantiated by a direct calculation which gives $\sigma_L = 4.5 \times 10^{-8}$ cm whereas Dennison's value (also based on the writer's values for $\int_0^\infty \mu(\nu)d\nu$) is $10.6\ 10^{-8}$ cm. The fact that kinetic theory estimates support the Lorentz value may perhaps be construed as deciding between Dennison's and Lorentz's analysis, but it is, of

[16] D. M. Dennison, Phys. Rev. **31,** 501, 1928

[17] From our point of view Dennison's demonstration amounts to recomputing the author's approximation function $(2b\psi_L(n))$ using the value of $\int_0^\infty \mu(\nu)d\nu$ derived by use of it and showing that it really does represent the experimental total absorption curve closely.

course, to be borne in mind that any collision broadening theory is necessarily only a qualitative guide.

It seems of importance to discuss the plausibility of the estimates of the characteristic constants associated with HCl which we have derived here. For this purpose we investigate the nature of the variation of the electrical moment $p(r)$ and effective charge $q(r)=p(r)/r$. We write

$$p(r)-p(r_0)=\frac{dp(r_0)}{dr}(r-r_0)+\frac{1}{2}\frac{d^2p(r_0)}{dr^2}(r-r_0)^2+\cdots$$

$$q(r)r-q(r_0)r_0=\left[\frac{dq(r_0)}{dr}r_0+q(r_0)\right](r-r_0)+\cdots \tag{11}$$

where r_0 refers to equilibrium position.

For the calculations of $dp(r_0)/dr$ given in Table II it was assumed that $(r-r_0)$ was harmonic[18] in t and the formulae used were based on Oppenheimer's quantum matrix expressions for the intensity of transition.[19] The most natural assumption[20] to make about HCl is that on adiabatic separation of the nuclei we should obtain H^+ and Cl^-. Hence it might seem plausible that $dq(r_0)/dr>0$ or by Eq. (11), $dp(r_0)/dr>q(r_0)$. The new quantum theory expression applied to Zahn's data on the dielectric constant of HCl leads[21] to $q(r_0)=0.818\times10^{10}$ which is practically equal to our value of[22] 0.86×10^{10} for $dp(r_0)/dr$. Since the precision limits of the integrated absorption coefficients are 25 percent or poorer it is even possible[23] that $dp(r_0)/dr<q(r_0)$ which would imply that adiabatic separation results in neutral H and Cl. We may say here only that $dq(r_0)/dr$ is not large.

A small positive value of $dq(r_0)/dr$ is also reconcilable with a separation into neutral atoms for, since the equilibrium position of the H nucleus is within the outer Cl shell, it may be that $dq(r)/dr$ becomes negative for r appreciably greater than r_0 only. It is pertinent to note the assignment of an atomic binding to HCl by Franck and Kuhn[24] on the basis of the nature of the dissociation as indicated by the absorption band limits.

[18] It may be shown that departure from the sine form would introduce higher order r derivatives of $p(r)$ and $q(r)$ in the relation between intensity and time rate of change of moment.

[19] J. R. Oppenheimer, Proc. Camb. Phil. Soc. **23,** 237 (1926). Cf. in this connection I, and Dennison's paper (reference 16).

[20] See for example E. C. Kemble, Journ. Opt. Soc. **12,** 1 (1926).

[21] Really because of the half quantum of vibrational energy in the zero state the notation $q(r_0)$ refers to the value of q for a larger value of r than r_0.

[22] The value of 0.86×10^{10} is not very different from that given in I. Dennison's recently published value of 0.95×10^{10} is based on the values of $\int_0^\infty\mu(\nu)d\nu$ given in I (which we have modified somewhat in this paper) and on a formal average of the absorption results for the various lines. The mean value is, however, not significant for the experimental measurements were capable of far greater precision in the cases of the lines $M=2$, 3, 4 than in any of the others.

[23] There are, of course, also the possibilities that our assumed line patterns were inapplicable or over-simplified or that there is some incorrectness in the theoretical formulae or physical constants used in determining $dp(r_0)/dr$ from $\int_0^\infty\mu(\nu)d\nu$.

[24] J. Franck and H. Kuhn, Zeits. f. Physik, **43,** 164 (1927).

Hence the value of $dp(r_0)/dr$ to be expected from the dielectric constant data is of the order of, or at most not very much greater than, $q(r_0)$, and is therefore in agreement with the estimates of $dp(r_0)/dr$ (and therefore of $\int_0^\infty \mu(\nu)d\nu$) given here. In this connection it is interesting to recall Van Vleck's test[25] of the suggested explanation for the incompatibility of the values of $\epsilon-1$ derived from optical data and dielectric constant measurements (namely the assumption that the consideration of the vibrational infra-red bands would bring the estimates into agreement). Actual computation, using the writer's value of $dp(r_0)/dr$ showed that the correction was far too small. The preceding discussion seems to dispose of the possibility that this value of $dp(r_0)/dr$ can be much too low[26] and supports Van Vleck's criticism.

We shall now take up Badger's[27] recent measurements on the rotation spectrum of HCl in the far infra-red. Inasmuch as Badger's findings are out of accord with theory, it seems of importance to see whether use of the more refined approximation methods described here may not indicate a fault in the working up of the data rather than in the data themselves. The approximation making use of the $n\psi_D(n)$ curve[28] yielded for the tangent at zero pressure the value 1.312×10^{-4} cm per cm of Hg pressure for a tube 77 cm long. Badger's computation gave 1.12×10^{-4} cm. The difference, though in the right direction, is too small to appreciably minimize the disagreement between theory and experiment.

It would no doubt be of value to apply the approximation methods illustrated above to the recalculation of the results of many other researches, for instance, to the determination of the intensities and intensity ratios of the Na doublets[29] (or Li or Cs, etc.). Here most of the data are for pressure variation and approximation functions of the form $n^s\psi(n)$ would lead to useful conclusions. In view of the contradictory nature of the many published results it would seem desirable to carry out an investigation for variable tube-length, since the interpretation then becomes somewhat simpler.

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[25] J. H. Van Vleck, Phys. Rev. **30,** 31 (1927).

[26] Certainly it is most unlikely that there is some unrecognized error in the data or deductions large enough to account for $dp(r_0)/dr$ being too small by a factor of 100.

[27] R. M. Badger, Proc. Nat. Acad. Sci. 408, 13 (1927). Note added July 9, 1928. In a recent conversation Dr. Badger mentioned unpublished work on NH_3 as supporting the view of a real difference between experimental intensities in the ultra-red and the predictions of existent theory.

[28] But see the remarks on p. 243.

[29] C. Fuchtbauer, Phys. Zeits. **12,** 722 (1911); R. Ladenburg, R. Minkowski, Zeits. f. Physik **6,** 153 (1921); B. Trumpy, Zeits. f. Physik **34,** 714 (1925), **40,** 594 (1926); W. Orthmann, Ann. d. Physik **78,** 607 (1925); W. Schutz, Zeits. f. Physik **25,** 299 (1924), etc.