

## THE SHAPE AND INTENSITIES OF INFRA-RED ABSORPTION LINES

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### ABSTRACT

An expression for the shape of an infra-red absorption line is developed on the basis that the principal factor in the broadening of a line is the limitation of the length of wave train a molecule may absorb due to its perturbation by thermal collisions. The shape of the line is accordingly found by expanding the finite wave train with a Fourier integral and then integrating over the distribution of lengths of wave train given by the kinetic theory of gases. The absorption coefficient as found in this way may be expressed to a high approximation by means of two damping curves involving the number of molecules per unit volume, the temperature, and  $\sigma$  the effective diameter.

To apply this result to the analysis of observed infra-red spectra allowance must be made for the low spectrometer resolution due largely to the wide slits employed. Two expressions are developed, holding for all but very weak lines, which relate the area under the absorption line  $Abs$ , the minimum value of the transmission  $T_{\min}$  and the true intensity  $\alpha$  with the slit width  $a$ , the cell length  $l$ , and the molecular constants.

$$Abs = [5.412\alpha n\sigma^2 l]^2 / [\pi h m]^2$$

$$Abs = -2.42a \log_{10} T_{\min}$$

It is shown that these formulae are capable of interpreting the absorption lines of the infra-red spectrum of HCl observed by R. F. Paton and yield a value of  $10.8 \times 10^{-8}$  cm for  $\sigma$ . The meaning of  $\sigma$ , the distance to which two molecules may approach without altering each others phases, as well as the range of validity of the assumptions is discussed and a correction to the absorption area formula for faint lines is deduced. In connection with a consideration of the absorption measurements of HCl by Kemble and Bourgin, a computation is made of the effective moving charge of the molecule giving the value  $\epsilon = (.199) 4.77 \times 10^{-10}$  E.S.U.

### INTRODUCTION

THE many observations which have been made of the infra-red absorption spectra of gases show clearly that the absorption lines are not confined to a single frequency but possess a definite shape and a finite width. A number of factors may be enumerated which combine to determine the form of the line: (a) Doppler effect; (b) an effect corresponding to the damping of a classical oscillator; (c) a resonance effect between neighboring molecules; (d) an effect due to the limitation of the length of the wave trains which may be absorbed by the molecules. The relative importance of these effects will depend largely upon the frequency being absorbed and upon the physical state of the gas. A simple calculation<sup>1</sup> shows that in the infra-red region,

<sup>1</sup> An estimate of the order of magnitude of effect (b) may be made by the following computation. A classical oscillator of frequency  $\nu$ , mass  $m$  and effective charge  $\epsilon$ , has a lifetime  $\tau$  due to damping, where  $\tau = 3c^3 m / 8\pi^3 \epsilon^2 \nu^2$ . The width of the corresponding absorption line  $\Delta\nu$  is given by  $\Delta\nu = 1/\tau$ . Setting in the appropriate values of the constants for the HCl

for normal temperatures and pressures, effects (a) and (b) are completely negligible in their influence upon the shape of the absorption lines although they may play an important role in determining the form of the high frequency x-ray lines. Holtzmark,<sup>2</sup> L. Mensing,<sup>3</sup> and others have met with considerable success in explaining the breadth of lines in the visible region of the spectrum on the basis of (c), the resonance effect between neighboring systems. This effect, while it may have some influence in determining the shape of the infra-red lines, appears to be of a smaller order of magnitude than (d) and we shall confine our attention in this paper to showing that this latter effect is capable of furnishing a satisfactory description of the infra-red absorption lines.

We may arrive at an expression for the form of an absorption line caused by a limitation of the wave train due to the thermal collisions with the following consideration which must hold as well in the new wave mechanics as in the classical mechanics. If the time during which a collision takes place between molecules is very short compared with the time  $t$  between collisions, the problem is identical with that of an undisturbed molecule upon which falls for a time  $t$  a radiation field  $\rho$ . If the radiation field  $\rho$  is uniform in frequency and if the molecule has a proper frequency  $\nu_0$ , the intensity with which it will absorb the frequency  $\nu$  is proportional to the square of the Fourier density integral

$$I_{\nu,t} = \left[ \int_0^{t/2} \cos(2\pi\nu x) \cos(2\pi\nu_0 x) dx \right]^2 = \frac{1}{4} \left[ \frac{\sin(\nu_0 - \nu)\pi t}{2\pi(\nu_0 - \nu)} + \frac{\sin(\nu_0 + \nu)\pi t}{2\pi(\nu_0 + \nu)} \right]^2.$$

Since the breadth of the line is in general very small compared with the frequency, we may neglect the second member and write,

$$I_{\nu,t} = \frac{\sin^2(\nu_0 - \nu)\pi t}{16\pi^2(\nu_0 - \nu)^2}.$$

The width of the absorption line as given by this expression is of the order  $1/t$  and for purposes of estimation, we may take  $t$  to be  $\bar{t}$ , the mean time between collisions. The kinetic theory of gases furnishes a relation between  $\bar{t}$ ,  $n$  the number of molecules per unit volume,  $\bar{c}$  the mean value of the velocity of each molecule, and  $\sigma$  the effective diameter of the molecule.

$$\bar{t} = 1/(2)^{1/2}\pi\sigma^2 n\bar{c}$$

The conception of a collision between two molecules which we must employ, is an encounter such that the phase of the molecules is sensibly altered

molecule and letting  $\epsilon = \alpha(4.77) \times 10^{-10}$  we find  $\Delta\nu = \alpha^2(1.1) \times 10^8$ . Remembering that  $\alpha$  is less than unity (about 1/5 for HCl) it will be seen that the broadening due to damping is far smaller than attributable to effect (d), in fact by a factor of about  $10^8$ .

<sup>2</sup> J. Holtzmark, Physik. Zeits. **25**, 73 (1924).

<sup>3</sup> L. Mensing, Zeits. f. Phys. **34**, 611 (1925).

leading to a limitation in the length of the wave train being absorbed.<sup>4</sup> The effective molecular diameter  $\sigma$  is the distance to which two molecules may approach without changing each others phases. It will presumably be of the order of magnitude generally found for molecular diameters and we may estimate it to have the value  $5 \times 10^{-8}$  cm. Setting this in we obtain  $\bar{t} = 2 \times 10^{-10}$  sec. The width of the line is then of the order  $\Delta\nu = 5 \times 10^9$  waves per sec. and corresponds in the HCl spectrum to about one hundredth the distance between consecutive lines. While this is from five to ten times smaller than the apparent width as observed by Imes<sup>5</sup> and others, we shall show that it is capable of explaining the experimental curves when the low spectrometer resolution is taken into account.

### 1. THE EQUATIONS GOVERNING THE ABSORPTION

As a rough approximation we might, as in the introduction, let  $t$  be the average time between collisions. A more exact expression may, however, be obtained by putting in the proportion of molecules whose time between collisions lies between  $t$  and  $t+dt$  and finally integrating over all values of  $t$ . The following expressions are well known from the kinetic theory of gases.

The proportion of molecules of velocity  $c$  having a path length lying between  $l$  and  $l+dl$  is  $e^{-l/\lambda_c} dl/\lambda_c$  where  $\lambda_c$ , the mean path length is given by,

$$\lambda_c = hmc^2/\pi^{1/2}n\sigma^2\psi(ch^{1/2}m^{1/2})$$

with

$$\psi(x) = xe^{-x^2} + (2x^2+1) \int_0^x e^{-y^2} dy$$

Here  $n$  is the number of molecules per unit volume,  $m$  the mass of each molecule and  $h = 1/2kT$ .

The proportion of molecules of velocity  $c$  having a time between collisions lying between  $t$  and  $t+dt$  is evidently  $e^{-ct/\lambda_c} cdt/\lambda_c$  and the proportion of all molecules having a time between collisions lying between  $t$  and  $t+dt$  is,

$$N_t = 4h^{3/2}m^{3/2}\pi^{-1/2} \int_{c=0}^{\infty} e^{-hmc^2 - ct/\lambda_c} (c^3/\lambda_c) dt dc$$

Let the total intensity with which light of frequency  $\nu$  is absorbed by molecules of proper frequency  $\nu_0$  be proportional to  $P$ , where  $P$ , is the extinction coefficient of the gas, expressed as a function of the frequency.

$$P_\nu = \int_0^\infty I_{\nu_i} N_i dt = \kappa \int_0^\infty \int_0^\infty e^{-hmc^2 - ct/\lambda_c} \frac{c^3 \sin^2(\nu_0 - \nu)\pi t}{\lambda_c(\nu_0 - \nu)^2} dc dt$$

<sup>4</sup> Clearly the whole calculation is founded upon the approximation usually employed in the kinetic theory of gases, namely that the molecules are impenetrable spheres of diameter  $\sigma$ , and may be expected to hold only in the region where the time between collisions is very much longer than the time of a collision.

<sup>5</sup> E. Imes. *Astrophys. Jour.* 50, 251 (1919).

The integration with respect to the time may be performed immediately giving,

$$P_\nu = 2\pi^2\kappa \int_0^\infty \frac{e^{-hmc^2}c^2dc}{(c^2/\lambda_2^2) + 4\pi^2(\nu_0 - \nu)^2}$$

By making the substitution  $x^2 = hmc^2$  we obtain,

$$P_\nu = \kappa' \int_0^\infty \frac{e^{-x^2}x^2dx}{(n^2\sigma^4\psi^2/4\pi hmx^2) + (\nu_0 - \nu)^2} \quad (1)$$

It is customary to designate the integral of the absorption coefficient  $P_\nu$  over all frequencies as  $\alpha$  the total intensity of absorption.<sup>6</sup>

$$\begin{aligned} \alpha &= \int_0^\infty P_\nu d\nu = \kappa' \int_0^\infty \int_0^\infty \frac{e^{-x^2}x^2dx d\nu}{(n^2\sigma^4\psi^2/4\pi hmx^2) + (\nu - \nu_0)^2} \\ &= 2\pi(\pi hm)^{1/2}(\kappa'/n\sigma^2) \int_0^\infty e^{-x^2}(x^3/\psi(x))dx. \end{aligned}$$

This last integral has already been evaluated by numerical quadrature.<sup>7</sup> Solving for  $\kappa'$  we find,

$$\kappa' = (2n\sigma^2\alpha/0.650\pi^{3/2}h^{1/2}m^{1/2})$$

Eq. (1) cannot be evaluated except by means of numerical quadrature. A large number of points found in this way shows, however, that the function,

$$y = \int_0^\infty \frac{x^2e^{-x^2}dx}{(\psi^2/x^2) + z^2}$$

may be represented with an accuracy greater than one per cent by means of the two equations:

$$y = (0.411/6.67 + z^2) \text{ from } z=0 \text{ to } z \cong 3$$

and

$$y = (0.440/7.60 + z^2) \text{ from } z \cong 3 \text{ to } z = \infty$$

Consequently the absorption coefficient  $P_\nu$  may be represented by

$$P_\nu = (1.244\alpha n\sigma^2/\pi^{3/2}h^{1/2}m^{1/2}) \frac{1}{(6.67n^2\sigma^4/4\pi hm) + (\nu - \nu_0)^2} \quad (1)'$$

from  $\nu - \nu_0 = 0$  to  $\nu - \nu_0 \cong (3n\sigma^2/2\pi^{1/2}h^{1/2}m^{1/2})$  and

<sup>6</sup> To integrate this function with respect to the frequency  $\nu$ , we replace  $\nu - \nu_0$  by  $y$  and integrate between the limits  $+\infty$  and  $-\infty$ . This procedure involves a certain approximation since while the upper limit of  $y$  is  $+\infty$ , its lower limit is really  $-\nu_0$ , but no appreciable error will be introduced since the integrand has become vanishingly small in this region. These remarks will also apply to some of the integrations which follow.

<sup>7</sup> Tait, Edin. Trans. **33**, 74 (1886).

$$P_\nu = (1.353\alpha n\sigma^2/\pi^{3/2}h^{1/2}m^{1/2}) \frac{1}{(7.60n^2\sigma^4/4\pi hm) + (\nu - \nu_0)^2} \quad (1)''$$

from  $\nu - \nu_0 \cong (3n\sigma^2/2\pi^{1/2}h^{1/2}m^{1/2})$  to  $\nu - \nu_0 = \infty$ . A certain test of the accuracy with which  $P_\nu$  is represented by these relations may be found by integrating them over all frequencies when it is found that,

$$\int_0^\infty P_\nu d\nu = (1.000)\alpha$$

The absorption coefficient  $P_\nu$  may be taken as representing the true shape of the spectral line where the transmission curve of such a line as determined by a spectrometer of infinitely high resolving power would be,

$$T_\nu = e^{-P_\nu l} \quad (2)$$

where  $l$  is of course the length of the absorption chamber.

The experimental measurements of the infra-red lines which have been made up to the present, however, have been made with instruments of low resolving power, where indeed the region of irresolution has been considerably greater than the true width of the line as given by Eq. (2). It is evident that the observed transmission curve will be intimately connected with the degree of resolution, that is, it will be governed by the broadness of the spectrometer slits as well as by the number of lines of the grating used.

Essentially the infra-red spectrometer (for example, that used by Imes) has the form shown in Fig. 1, where the light after passing through the

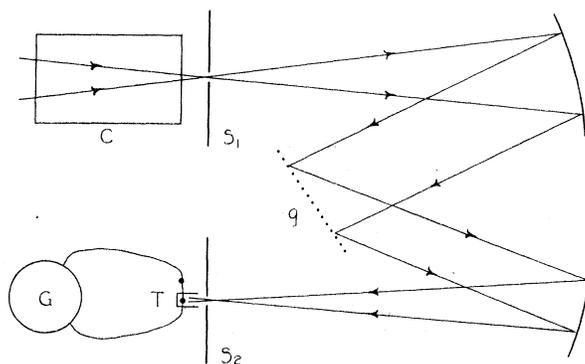


Fig. 1

absorption cell  $C$  is defined by a slit  $s_1$ , of width  $a$ . After being diffracted by the grating  $g$ , it passes through a further slit  $s_2$  of width  $b$  and falls upon the thermopile  $T$ . We may now define the resolution of the spectrometer by saying that the intensity with which the thermopile receives a frequency  $\nu$  is  $\rho_\nu$ , where  $\nu_i$  is the computed frequency falling on the thermopile, (i.e. that frequency which the thermopile would receive if the spectrometer had an infinitely high degree of resolution). The percentage transmission recorded by the instrument at the frequency  $\nu_i$  is now

$$T_{\nu_i} = \frac{\int_0^{\infty} \rho_{\nu_i} e^{-P\nu l} d\nu}{\int_0^{\infty} \rho_{\nu_i} d\nu} \quad (3)$$

The form of  $\rho_{\nu_i}$  is dependent upon the resolution of the grating and upon the widths of the slits  $s_1$  and  $s_2$ . Assuming the intensity of the source of radiation to be independent of the frequency, that is, that the background is uniform over the region of the line, we may consider two separate cases.

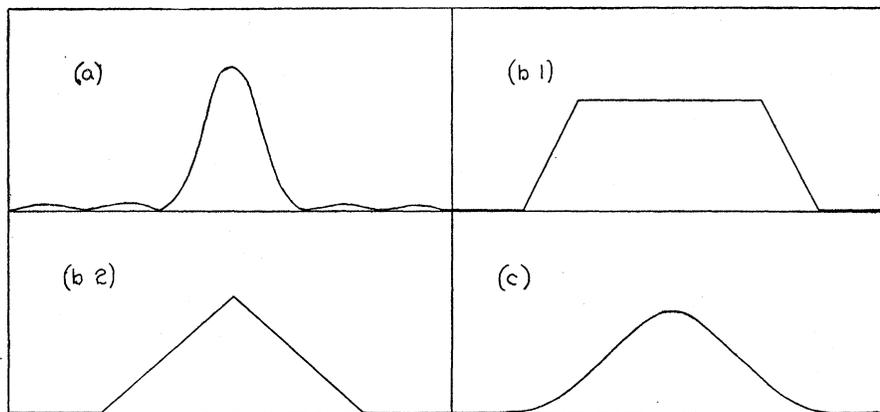


Fig. 2

(a) Let the slits be both infinitely narrow, in which case  $\rho_{\nu_i}$  is determined by the number of lines of the grating used,  $m$ , and the order of the spectrum,  $n$ . From optical theory we have the following expression for  $\rho_{\nu_i}$  which is reproduced in Fig. 2(a).

$$\rho_{\nu_i} = \frac{\sin^2 \left\{ (\nu_i - \nu) \pi mn / \nu_i \right\}}{(\nu_i - \nu)^2}$$

The degree of resolution of the grating has been defined as the distance from the central maximum to the first minimum.

$$\delta\nu = \nu_i / mn$$

(b) The second case which we may consider is that where the grating has perfect resolution,  $m = \infty$  but where the slits have a finite width. In general, we might suppose them to be unequal with  $a > b$ . It may then be shown that  $\rho_{\nu_i}$  is constant from

$$\nu = \nu_i - a/2 + b/2 \text{ to } \nu = \nu_i + a/2 - b/2$$

from which points it decreases linearly to zero at  $\nu_i + (a+b)/2$  and  $\nu_i - (a+b)/2$  respectively, as pictured in Fig. 2 (b1). When the two spectro-

meter slits are made equal,  $a = b$ , the distribution  $\rho_{\nu_i}$  assumes the triangular form shown in Fig. 2 (b2).

It appears that in most of the work done in the infra-red region, the degree of resolution of the grating is higher than that afforded by the width of the slits. Imes, for example, gives the figures

$$\delta\nu = 0.39 \times 10^{10} \text{ waves per sec.}$$

whereas he states that at the center of the HCl band

$$a = b = 7.3 \times 10^{10} \text{ waves per sec.}$$

It seems very probable, therefore that  $\rho_{\nu_i}$  has a form similar to Fig. 2 (b2) but rather softened by the irresolution of the grating as shown in Fig. 2 (c). Such a curve appears to be very similar to a Gauss error curve and various estimates show that the Gauss curve may be used for  $\rho_{\nu_i}$  without introducing any considerable errors. In this case we let

$$\rho_{\nu_i} = e^{-(\nu_i - \nu)^2 (2.77)/a^2} \quad (4)$$

where the constant 2.77 is introduced in order that the half-value of  $\rho_{\nu_i}$  may coincide with the corresponding point of the curve  $b$  (2). Setting this value into Eq. (3) we have

$$T_{\nu_i} = (2.77/\pi a^2)^{1/2} \int_0^\infty e^{-P\nu l - 2.77(\nu_i - \nu)^2/a^2} d\nu \quad (5)$$

This expression, with the aid of Eqs. (1)' and (1)'' defining  $P_\nu$ , determines the shape and intensity of the observed absorption lines and may be evaluated by numerical quadrature. A particular value of the transmission, namely its minimum value, can be expressed as an explicit function of the constants by introducing an approximation for  $P_\nu$ . For lines where the maximum absorption is not too small, an examination of the magnitude of the constants shows that (1)' and (1)'' may be replaced by

$$P_\nu = \frac{1.353\alpha m \sigma^2}{\pi(\pi h m)^{1/2}(\nu - \nu_0)^2} \quad (1)'''$$

The validity of this approximation rests on the fact that for small values of  $\nu - \nu_0$  where (1)''' is sensibly different from (1)' and (1)'', the integrand of (5) has already become vanishingly small. In the last section of this paper the errors of the approximation (1)''' will be discussed. Using the above substitution the observed transmission at the point  $\nu_i$  will be

$$T_{\nu_i} = (2.77/\pi a^2)^{1/2} \int_0^\infty \exp \left[ -\frac{1.353\alpha m \sigma^2 l}{\pi(\pi h m)^{1/2}(\nu - \nu_0)^2} - \frac{2.77(\nu - \nu_i)^2}{a^2} \right] d\nu \quad (5)'$$

This equation determines the shape of the line and may be integrated at the center of the line where  $\nu_i = \nu_0$ . The minimum value of the transmission is accordingly,

$$T_{min} = \exp \left[ -2(1.194\alpha n \sigma^2 l)^{1/2}/a(\pi h m)^{1/4} \right] \quad (6)$$

or taking the logarithm of  $T_{\min}$  to the base 10 we find,

$$(\log_{10} T_{\min})^2 = 0.520\alpha n\sigma^2 l / a^2 (hm)^{1/2} \quad (6)'$$

An expression for the total area under the absorption curve,  $Abs$ , may be obtained which will be found to be independent of the form of  $\rho_{\nu_i}$ .

$$Abs = \int_0^\infty (1 - T_{\nu_i}) d\nu_i = \int_0^\infty \left\{ 1 - \frac{\int_0^\infty \rho_{\nu_i} e^{-P\nu_i} d\nu_i}{\int_0^\infty \rho_{\nu_i} d\nu_i} \right\} d\nu_i$$

In general the distribution of frequencies reaching the thermopile will be symmetrical about  $\nu_i$  and will depend only upon the absolute magnitude of  $\nu - \nu_i$ . In that case we may integrate the second member on the right hand side of the equation with respect to  $\nu_i$  and obtain,

$$Abs = \int_0^\infty d\nu_i - \int_0^\infty e^{-P\nu_i} d\nu_i$$

The variable  $\nu_i$  may now be changed to  $\nu$  without altering the value of the expression. The final integration may be readily performed if we use the approximate expression (1)''' for  $P_\nu$ .

$$Abs = (5.412\alpha n\sigma^2 l)^{1/2} / (\pi hm)^{1/4} \quad (7)$$

By combining Eqs. (6)' and (7) we may obtain a relation between the area under the absorption curve, the maximum value of the absorption and the slit width  $a$ .

$$Abs / |\log_{10} T_{\min}| = 2.42a \quad (8)$$

Eq. (6) has been found by introducing into (3) a simplified expression for  $P_\nu$  and for  $\rho_{\nu_i}$ , the Gaussian error curve. An idea of the sensitiveness of (3) to the form of  $\rho_{\nu_i}$  may be gained by assuming that the grating employed has infinitely good resolution and that the slits  $s_1$  and  $s_2$  have the same width,  $a$ . That is, we may use instead of the error curve, the triangular intensity distribution shown in Fig. 2 (b2). We then have

$$T_{\nu_i} = \frac{\int_{\nu_i-a}^{\nu_i} (a - \nu_i + \nu) e^{-P\nu_i} d\nu}{\int_{\nu_i-a}^{\nu_i} (a - \nu_i + \nu) d\nu}$$

In the particular case of the center of the line, where  $\nu_i = \nu_0$  and where we use the approximate expression (1)''' for  $P_\nu$  we find,

$$T_{\min} = (2/a^2) \int_0^a (a-x) e^{-p^2/x^2} dx \quad (9)$$

where  $x = \nu - \nu_0$ , and  $p^2 = 1.353\alpha n\sigma^2 l / \pi (\pi hm)^{1/2}$ . This definite integral may be expanded in a series which is rapidly convergent for values of  $p/a \leq 1$ .

$$\begin{aligned}
T_{\min} = e^{-p^2/a^2} - 3.545(p/a) & \left\{ 1 - (2/\pi^{1/2}) \int_0^{p/a} e^{-x^2} dx \right\} \\
& + (p^2/a^2)(\log(a^2/p^2) - 0.5772) + p^4/a^4 - p^6/2 \cdot 2!a^6 \\
& + p^8/3 \cdot 3!a^8 - \dots
\end{aligned} \tag{9}'$$

A comparison of (6) and (9)' shows that the two are in almost perfect agreement for values of  $T_{\min}$  between 1. and 0.5 (i.e., between zero and fifty percent absorption), at  $T_{\min} = 0.3$  the divergence is about 1 percent at 0.1 about 5 percent and even below this the divergence is not very great.

The substantial agreement between Eqs. (6) and (9)' over the majority of their ranges shows that in interpreting most of the observed infra-red absorption lines, we may employ either the Gaussian or the triangular distribution for  $\rho_{\nu_i}$  without introducing serious errors.

## 2. THE ANALYSIS OF EXPERIMENTAL ABSORPTION CURVES

We propose to apply the equations developed in the preceding section to an analysis of the infra-red spectrum of HCl.<sup>8</sup> Although a great many observations of these lines have been made, the majority are unsuited to our purpose since they were made with the intention of determining the positions of the lines with great accuracy rather than their intensities.

A set of measurements which appears to be very satisfactory as regards the determination of intensity was taken by Dr. R. F. Paton<sup>9</sup> and I am greatly indebted to him for the use of his original data and curves. Paton observed the infra-red spectrum of HCl for three different temperatures of the gas, 20°C, 100°C, and 250°C, using the same spectrometer arrangement that Imes had used but with somewhat shorter absorption cells. The curves taken at the lower temperatures present a series of regular lines between which the absorption falls to a low value if not completely to zero. The third curve taken at 250°C shows several obvious irregularities in the absorption intensities presumably due to the greater experimental difficulties involved and we shall accordingly confine our attention to the lower temperature curves.

Many sources of error tend to make an accurate determination of the form of the absorption lines very difficult and a study of Paton's data reveals that the areas of absorption deduced from his curves may be in error by amounts of the order of 10 percent. The very faint lines at either end of the band have not been included in the present analysis since both the observational error is greatest for them and also the approximation of Eq. (1)''' for  $P_{\nu}$  will hold least well.

The observed spectrum of HCl at 20°C, plotted as a function of the relative absorption and  $\theta$  the angle of the grating was planimetered and the

<sup>8</sup> A certain error will no doubt exist since the HCl lines are not single as demanded by our theory but each is accompanied by a weaker satellite due to the isotope effect of the Cl. The effect of two lines close together is, in first approximation at least, merely additive as the consistency and freedom from systematic error of our results show.

<sup>9</sup> R. F. Paton, Phys. Rev. 15, 541 (1920).

areas under each line in the square unit of relative absorption times grating angle appear in the second column of Table I. The third column contains  $T_{\min}$ , the value of the relative transmission at the center of the line and the fourth column shows the absorption area divided by the absolute value of the logarithm of  $T_{\min}$  to the base 10. The values in column four appear to be

TABLE I

*Calculations based on Paton's absorption curves for HCl at 20°C. Tube length = 4 cm; temperature = 20°C; atmospheric pressure.*

Line No.	Abs $\times 10^2$	$T_{\min}$	Abs $\times 10^2$		$K\alpha$	Abs
			$-\log_{10} T_{\min}$	Abs		$(K\alpha)^{1/2}$
-8	3.28	0.49	11.1	2.36	0.236	4.85
-7	5.43	.32	11.0	4.01	.460	5.92
-6	7.58	.20	10.8	5.71	.786	6.45
-5	8.65	.16	10.9	6.65	1.184	6.10
-4	10.32	.115	11.0	8.11	1.560	6.49
-3	9.51	.10	9.51	7.71	1.722	5.87
-2	8.71	.14	10.2	7.10	1.524	5.75
-1	6.56	.20	9.3	5.43	.920	5.66
+1	7.80	.165	10.0	6.71	.975	6.80
+2	10.11	.10	10.1	8.83	1.720	6.73
+3	9.14	.10	9.1	8.12	2.055	5.66
+4	8.34	.10	8.3	7.51	1.96	5.37
+5	7.42	.13	8.4	6.78	1.59	5.37
+6	7.26	.205	10.6	6.71	1.114	6.35
+7	5.49	.30	10.5	5.14	.688	6.20
+8	3.55	.45	10.3	3.37	.365	5.59

nearly constant in agreement with Eq. (8) and the non-systematic variations which do occur may without doubt be ascribed to the experimental errors. By setting the average value, 10.1, into Eq. (8) we obtain the slit width  $a$  in terms of the grating angle  $\theta$ , or from the grating equation in terms of frequency.

$$\delta\theta = 2.50' ; \quad \delta\nu = 10.5 \times 10^{10}$$

Paton does not explicitly give the slit width that he used but the above values are of the correct order of magnitude. It appears at first a little strange that our computed value for  $\delta\nu$  is somewhat larger than Imes' slit width of  $7.3 \times 10^{10}$ , whereas a general inspection of Imes' and Paton's curves indicates that the latter must have used the same if not narrower slits. The explanation for this probably lies in the fact that the real distribution of intensity  $\rho_{\nu_i}$  entering the thermopile may be somewhat larger than the  $\rho_{\nu_i}$  computed from the slit widths due to inaccuracies in the focus or in the optical system.

The fifth column of Table I contains the area under each band line in the units of relative absorption times waves per cm. This may readily be found from the grating equation, the frequency being taken sensibly constant over the region of each line.

$$\lambda = K \sin \theta ; \quad \delta\nu = [K^2\nu^4 - \nu^2]^{1/2}\delta\theta$$

where  $K = 6.7682\mu$  according to Paton's data.

The sixth column of Table I contains numbers proportional to the theoretical intensities of the fundamental vibration rotation band lines of HCl at a temperature of 20°C as computed by a method to be described in the next paragraph. From Eq. (7) the total area of absorption is seen to be proportional to the square root of  $\alpha$ , the true intensity of the line. Accordingly the value of  $Abs/(k\alpha)^{1/2}$  has been tabulated (column seven) and appears to be constant within the limits of error. Here, as in the fourth column of the table, it is very satisfactory that the divergences from constancy are of the accidental sort and are not systematic.

The theoretical intensities will be given by the following relation<sup>10</sup>

$$\alpha_j^i = 2\pi^3 N_i \nu_j^i g_j (\epsilon a_i^i)^2 / 3hc g_i$$

where the intensity  $\alpha_j^i$  is the integral of the absorption coefficient over the region of the line corresponding to a transition from the  $i$ th to the  $j$ th quantum state.  $N_i$  is the number of molecules in the  $i$ th state,  $\nu_j^i$  the frequency of the transition and  $g_j$  and  $g_i$  are the weights of the  $j$ th and  $i$ th states respectively.  $\epsilon a_i^i$  is the amplitude of the electric moment of a transition from the  $j$ th to the  $i$ th states which before the advent of the new mechanics had to be taken as some undetermined mean of the classical amplitudes in these two states.

Oppenheimer<sup>11</sup> has derived, on the basis of the matrix mechanics, the amplitudes of the lines in the fundamental band of an anharmonic vibrator rotator and gives, (under a somewhat different notation)

$$\begin{aligned} \left( \begin{matrix} 1 & m-1 \\ a & m \end{matrix} \right)^2 &= \frac{h}{2\pi^2 \mu \nu_0} \left( \frac{m}{2m-1} \right) \left( 1 + 4\gamma m \left( 1 + \frac{5}{8}\gamma m - \frac{3}{8}\gamma \right) \right) \\ \left( \begin{matrix} 1 & m \\ a & m-1 \end{matrix} \right)^2 &= \frac{h}{2\pi^2 \mu \nu_0} \left( \frac{m}{2m+1} \right) \left( 1 - 4\gamma m \left( 1 - \frac{5}{8}\gamma m - \frac{3}{8}\gamma \right) \right) \end{aligned}$$

where  $m = 1, 2, 3, \dots$ ; and  $\gamma = h/4\pi^2 I \nu_0$

$I$  is the moment of inertia of the unexcited molecule and  $\nu_0$  the normal frequency of vibration.

These quantities may be substituted into equation (10) giving for example the intensities of the lines in the negative branch.

$$\alpha_{1m-1}^{0m} = \frac{\pi \epsilon^2 \nu m e^{-W m / kT} F}{3c\mu \sum_0^{\infty} (2m+1) e^{-W m / kT}}$$

where

$$\begin{aligned} F &= \frac{\nu_{1m-1}^{0m}}{\nu_0} \left( 1 + 4\gamma m \left( 1 + \frac{5}{8}\gamma m - \frac{3}{8}\gamma \right) \right) \\ g_m &= 2m+1 \end{aligned}$$

<sup>10</sup> See for example D. M. Dennison, *Phil. Mag.* **1**, 195 (1926).

<sup>11</sup> J. R. Oppenheimer, *Proc. Camb. Phil. Soc.* **23**, 327 (1926).

and

$$N_m = \frac{n(2m+1)e^{-W_m/kT}}{\sum (2m+1)e^{-W_m/kT}}$$

In the sixth column of Table I we have tabulated the values of  $K\alpha$ ,<sup>12</sup>

$$K\alpha = me^{-W_m/kTF} \quad (11)$$

using the work of Colby, Meyer, and Bronk<sup>13</sup> to determine the energy and the frequencies entering  $F$ . The constant  $K$  has then the value,

$$K = 3c\mu \sum_0^{\infty} (2m+1)e^{-W_m/kT} / \pi\epsilon^2 n \quad (12)$$

Kemble and Bourgin<sup>14</sup> have arrived at values for the true absorption  $\alpha$  by observing the lines with a series of different absorption cells of varying length. They plotted the integral of the apparent absorption coefficient over the line against the cell length and extrapolated to zero cell length. This procedure may be justified by remembering that if the cell length is short and the absorption small, the apparent absorption coefficient  $\log T_{\nu_i}/l$  may be replaced by  $(1 - T_{\nu_i})/l$ . Its integral over the line we have shown to be

$$(1/l) \int_0^{\infty} (1 - T_{\nu_i}) d\nu_i = (1/l) \int_0^{\infty} (1 - e^{-P\nu^l}) d\nu$$

If  $l$  is very small  $e^{-P\nu^l}$  may be developed and only the first two terms retained giving,

$$(1/l) \int_0^{\infty} P\nu^l d\nu = \alpha$$

by definition.<sup>15</sup>

In Table II we have given in the second column our values of  $K\alpha$  and in the third column, the experimental values of  $\alpha$  as observed by Kemble and Bourgin. The last column, the quotient of the two preceding columns is seen to be very nearly constant with an average value of,  $K = 4.00 \times 10^{-12}$ .<sup>16</sup>

<sup>12</sup> A corresponding expression  $K\alpha = F'me^{-W(m-1)/kT}$  gives the intensities of the lines of the positive branch.

<sup>13</sup> Colby, Meyer, and Bronk, *Astrophys. Journ.* **57**, 7 (1923).

<sup>14</sup> E. C. Kemble and D. G. Bourgin, *Nature* **117**, 789 (1926).

<sup>15</sup> In Eq. (7) we have shown  $\int_0^{\infty} (1 - T_{\nu_i}) d\nu_i$  to be proportional to the square root of  $\alpha$  instead of to  $\alpha$  as here. This is of course due to the fact that Eq. (7) is based on an approximate expression for  $P\nu^l$  which does not hold when the maximum value of  $P\nu^l$  is small.

<sup>16</sup> In a recent paper (*Phil. Mag.* **1**, 195, 1926) the author attempted to compute the effective charge  $\epsilon$  through the absolute absorption of the near infra-red bands. His estimates of the absorption were considerably too small due to the influence of the large slit widths used by the experimenters. The value of  $\epsilon$  may now be more accurately computed by means of Eq. (12) using  $K = 4.00 \times 10^{-12}$ . This yields  $\epsilon = (0.199) \times 4.77 \times 10^{-10}$  E.S.U., which may be compared with the effective charge  $\epsilon'$  obtained by dividing the permanent electric moment

TABLE II

Line No.	$K\alpha$	$\alpha \times 10^{-10}$	$K \times 10^{12}$
-6	0.786	22.55	3.49
-5	1.184	29.62	3.99
-4	1.560	37.62	4.15
-3	1.722	41.25	4.17
-2	1.524	37.48	4.06
-1	.920	23.78	3.87
+1	.975	24.50	3.98
+2	1.720	41.8	4.11
+3	2.055	49.0	4.20
+4	1.96	47.0	4.17
+5	1.59	37.9	4.20
+6	1.114	26.6	4.19
+7	.688	16.32	4.21
+8	.365	9.06	4.03
+9	.182	4.60	3.96
+10	.0768	2.35	3.27

We are now in a position to compute  $\sigma$ , the effective diameter of the HCl molecule. The average value of the seventh column of Table I is 5.95, whence, in waves per second,

$$Abs/\alpha^{1/2} = 11.9 \times 10^{-6} \times 3 \times 10^{10}$$

Introducing this value into Eq. (7) we find

$$\sigma = 10.6 \times 10^{-8} \text{ cm}$$

The value for  $\sigma$  just obtained is essentially larger than the distance between the nuclei which from band spectra data has been found for HCl to be  $1.26 \times 10^{-8}$  cm.<sup>17</sup> This result is by no means inconsistent with our theory since the diameter  $\sigma$  entering our equations is that minimum distance to which a molecule may approach another molecule without altering its phase, that is, without interrupting its wave train. It is very probable that for a highly dipol molecule such as HCl,  $\sigma$  will be considerably greater than the nuclear separation. Before discussing this question further, we shall proceed to examine Paton's second curve.

This curve, taken at the temperature of 105°C, contains somewhat more lines than the 20°C curve, and is represented by the data in Table III. The fourth column seems again to be sensibly constant and has the average value 8.7, yielding the following values for the slit width expressed in degrees or in waves per second.

$$\delta\theta = 2.16' ; \delta\nu = 9.1 \times 10^{10}$$

by the distance between the nuclei. Using C. T. Zahn's (Phy. Rev. **24**, 400 (1924)) measurements of the electric moment, we find  $\epsilon' = 1.03 \times 10^{-18} / 1.265 \times 10^{-8} = (0.171) \times 4.77 \times 10^{-10}$ . While these two values  $\epsilon$  and  $\epsilon'$  are of the same order of magnitude, there is no reason to suppose that they should be exactly equal since they are a measure of quite different properties of the molecule for which the "effectiveness" of the true distribution of charge need not be the same.

<sup>17</sup> The molecular diameter as determined from viscosity measurements is of course also much larger than the nuclear separation and has a value of about  $5 \times 10^{-8}$  cm.

Patons' data do not show any evidence of the spectrometer or slit adjustment being changed between the taking of the 20° and the 105° curve although the difference between 2.50' and 2.16' seems a little too great to be wholly attributable to the experimental error in the curves.

The fifth column of Table III contains the area under the absorption curve measured in relative absorption times waves per cm and the sixth column has a set of values proportional to the theoretical intensities as defined

TABLE III

*Tube length = 6 cm; temperature = 105°C; atmospheric pressure.*

Line No.	Abs×10 <sup>2</sup>	T <sub>min</sub>	Abs×10 <sup>2</sup>		Kα	Abs
			-log <sub>10</sub> T <sub>min</sub>	Abs		
-10	2.10	.59	9.2	1.45	.140	5.61
-9	3.12	.44	8.8	2.20	.278	5.92
-8	4.35	.35	9.5	3.15	.505	6.13
-7	5.48	.25	9.1	4.06	.827	6.03
-6	6.08	.14	7.1	4.59	1.233	5.47
-5	8.23	.14	9.6	6.34	1.634	6.44
-4	8.50	.11	8.9	6.69	1.930	6.11
-3	8.71	.12	9.5	6.99	1.961	6.21
-2	7.80	.135	9.0	6.36	1.624	6.11
-1	6.30	.175	8.3	5.23	.937	6.51
+1	5.21	.19	7.2	4.48	.975	5.28
+2	7.80	.12	8.5	6.83	1.753	5.89
+3	8.45	.10	8.5	7.50	2.190	5.70
+4	8.77	.11	9.2	7.90	2.230	5.87
+5	8.28	.135	9.5	7.55	1.965	5.90
+6	5.97	.20	8.6	5.53	1.538	4.81
+7	5.16	.25	8.5	4.83	1.080	4.97
+8	2.96	.42	7.9	2.81	.655	3.66
+9	1.88	.56	7.5	1.80	.389	3.02
+10	1.77	.66	9.8	1.72	.203	3.93

by Eq. (11). In computing the molecular diameter from the average value 5.48 of the seventh column we must remember that  $K$ , the proportionality factor, is a function of the temperature. In fact from equation (12),

$$\frac{K_1}{K_2} = \frac{n_2 \sum_0^{\infty} (2m+1) e^{-W m/kT_1}}{n_1 \sum_0^{\infty} (2m+1) e^{-W m/kT_2}}$$

from which we obtain the value,

$$K_{378} = (1.65) K_{293} = 6.62 \times 10^{-12}$$

The absorption area divided by the theoretical intensity is then given by

$$Abs/\alpha^{1/2} = 14.1 \times 10^{-6} \times 3 \times 10^{10} \text{ waves/sec.}$$

The molecular diameter may be computed as before through the use of Eq. (7); we obtain

$$\sigma = 11.0 \times 10^{-8} \text{ cm}$$

in good agreement with the value previously determined from the 20°C curve.

### 3. DISCUSSION

The very satisfactory manner in which the equations of §1 have interpreted the experimental curves of Paton leaves little doubt but that they are of the correct general form. The agreement of itself however does not guarantee the correctness of the meanings we have given to the constants of the formulae. From the fact that the molecular diameter of HCl as computed from the observed absorption, is of the expected order of magnitude we may conclude that the limitation of wave trains due to collisions is at least one of the principal factors in broadening the absorption lines. On the other hand the interaction of elastic spheres upon which conception the equations of §1 are based would appear to be somewhat inadequate to describe the state of the gas except in the limiting case where the mean free path  $\lambda$  is very long compared with  $\sigma$ . A simple computation shows that this is hardly true in the experiments of Paton, for  $\lambda/\sigma = 1/2^{1/2}\pi n\sigma^3$ , whence, substituting the value of  $\sigma$  and  $n$ , the number of molecules per unit volume, we find,  $\lambda/\sigma \cong 9$ . A series of observations of the absorption with the gas at reduced pressure would indicate with what accuracy our value of  $\sigma$  represents the effective distance to which two molecules may approach without perturbing each others wave trains.

Leaving the question of the interpretation of the constants and returning to the assumption that our formulae give the correct form of the absorption we notice that Eqs. (6)' and (7) should be of very general use since they allow us to compare the relative intensities of a set of lines. A correction term may be applied to Eq. (7) for analyzing absorption curves whose maximum absorption is small. Eq. (7) is based on the approximate expression (1)''' for  $P_\nu$  and has the form,

$$Abs = \int_{-\infty}^{+\infty} (1 - e^{-a^2/x^2}) dx = 2a\pi^{1/2}$$

where  $a^2 = 1.353\alpha n\sigma^2 l / \pi(\pi h m)^{1/2}$ .

For absorption lines whose maximum value of  $P_\nu$ ,  $l$  is not large we must represent  $P_\nu$  by Eq. (1)'' in which case we obtain the following approximate expression for the absorption area.<sup>18</sup>

<sup>18</sup> An exact calculation would of course involve both Eqs. (1)' and (1)'' but the error introduced by using Eq. (1)'' alone will certainly not be appreciable in the first order correction terms and probably not even in the second.

$$Abs = \int_{-\infty}^{+\infty} (1 - e^{-a^2/(b^2+x^2)}) dx \quad (13)$$

$$= 2a(\pi)^{1/2} \left( 1 - \frac{b^2}{4a^2} - \frac{3}{32} \frac{b^4}{a^4} - \dots \right) + \left( \frac{11}{8} \frac{b^3}{a^2} + \dots \right) e^{-a^2/b^2}$$

where

$$b^2 = 7.60n^2\sigma^4/4\pi hm$$

Substituting the values of the constants we find that the corrections to the data of Table I are within the experimental error, for example, the correction to the strong lines such as +3, is about 0.3% whereas the largest correction (to the weakest line, -8) is only 2.7%. No doubt errors of this same order of magnitude are incurred by using the approximation (1)''' to obtain Eq. (6)', the relative transmission at the center of the line.

No attempt has been made in the present paper to compare the observed shapes of the absorption lines with the shape determined by Eq. (5) since the experimental observations now available do not appear to be sufficiently accurate to make such a comparison fruitful. A few points have, however, been computed by numerical quadrature for a particular line and these agree with the observed points to within the experimental error.

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*Note added in proof. February 28, 1928.* Unfortunately no discussion has been included in the above paper of a very interesting article by D. G. Bourgin (Phys. Rev. V. 29, p. 794, (1927)) which gives a detailed exposition of the experimental work underlying the Bourgin and Kemble letter to Nature (l.c.). These new data appear to be completely in accord with the theoretical formulae we have developed. In Table I, Bourgin gives the variation of the absorption area with tube length which may be compared with our Eq. (13). Selecting two representative lines +1 and +4, we construct the following table where the second and fourth columns contain Bourgin's values converted into the units of relative absorption times waves per cm and the third and fifth columns the corresponding computed values letting  $\sigma = 10.8 \times 10^{-8}$  cm. The agreement is satisfactory.

Tube length	+1 Abs	Comp.	+4 Abs	Comp.
2.97	4.81	5.27	6.28	7.17
.996	3.13	2.97	4.35	4.08
.54	2.34	2.14	3.38	2.63
.248	1.42	1.38	2.15	1.96
.169	1.08	1.06	1.64	1.57
.0988	.725	.737	1.16	1.11

In Fig. 6A, Bourgin shows the change in maximum absorption coefficient for the line +3 with tube length. His curve appears to fall very close to the values predicted by our Eq. (6) if the spectrometer slit width is taken as  $a = 14 \times 10^{10}$  waves/sec. Bourgin does not explicitly give the slit width in frequency units but from his Fig. 3 it appears to be of this order of magnitude.

Using the experimental intensities of the lines +1 and -1 together with the simple formula for the Einstein coefficients, Bourgin computes the effective moving charge to be  $\epsilon = (.173) \times 4.77 \times 10^{-10}$ . We believe our value of  $\epsilon = (.199) \times 4.77 \times 10^{-10}$  to be somewhat more accurate since it is based on the mean of the experimental intensities of all the lines from -6 to +10, and since the theoretical formulae of Oppenheimer which we use take into account the perturbations between the anharmonic vibration and the rotation.