

LINE INTENSITIES IN THE HYDROGEN CHLORIDE
FUNDAMENTAL BAND¹

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ABSTRACT

Absorption intensities in the lines of the HCl fundamental band for tube-lengths from 0.0998 to 2.97 cm.—The transmission of columns of HCl 0.0998, 0.169, 0.248, 0.54, 0.996, and 2.97 cm long in the region of its fundamental vibration-rotation band at 3.5μ was measured with a bismuth-silver vacuum thermopile. The light was resolved by a quartz spectrometer. The curves give indirect evidence of the isotopic doubling and yield fairly accurate absolute and relative values of the intensities of the absorption lines. The values given are checked by several independent methods of calculation. The results confirm the predicted asymmetry in the intensities of corresponding lines in the *P* and *R* branches as suggested by Kemble's theory, the summation rule, and the new formulation of the quantum theory, and, further, verify the quantitative predictions of these theories when the statistical weights are suitably chosen. The particular choice favored by the data is the selection $p_M = 1, 3, 5, \dots$, if the lines are assumed to be singlets (and $p_M = 2, 4, 6, \dots$, if the lines are assumed to be spectroscopic doublets on the presumption that the summation rule is valid for this case). The lines are apparently narrower and deeper than heretofore supposed, and it is demonstrated that the exponential law of transmission is not applicable to the transmission curves even after these have been corrected by the usual slit-width correction formulas.

Einstein probability-of-transition coefficients.—The calculated values of the Einstein probability-of-transition coefficients are $B_{0,1} = 5.1 \times 10^{16}$ for the first line of the positive branch and $A_{0,1} = 58$ for the first line of the negative branch. These values are in harmony with estimates based on the correspondence principle.

Variation of the molecular moment with nuclear displacement.—The most plausible value of the variation of the molecular moment with nuclear displacement as determined for the region of the equilibrium position is 0.828×10^{-10} e.s.u. The combination of the measurements of this paper with Zahn's data on the dielectric constant of HCl yields more reasonable results when the calculations are made in accordance with the new quantum theory or classical theory than when the older forms of the quantum theory are used.

INTRODUCTION

THE recent and more precise developments of the quantum theory have focussed attention on the intensities of spectral lines in emission and absorption. Although the pioneer experiments at Utrecht and elsewhere have afforded intensity data for atomic systems, it appears that no corresponding quantitative work from this point of view has been done in the molecular field. The experimental part of this paper presents the results of an investigation of the absorption lines of HCl in the region of its fundamental band in the infra-red at 3.5μ .

¹ E. C. Kemble and D. G. Bourgin, *Nature* **117**, 789 (1926); D. G. Bourgin and E. C. Kemble, *Phys. Rev.* **27**, 802 (1926).

In accordance with general usage, the term absorption intensity of a line M is taken to mean the integral of the absorption coefficient taken over the absorption line and is written

$$\alpha_M = \int_M \mu(\nu) d\nu \quad (1)$$

where $\mu(\nu)$ is the absorption coefficient expressed as a function of the frequency. The subscript M takes on negative values for the P branch of the band and particularizes the M th line counting from the missing central component.

Absorption curves for the HCl fundamental band have been obtained for long tube-lengths by several experimenters.² The most accurate results are those of Imes³ and of Brinsmade and Kemble⁴ whose researches were carried out primarily to determine the positions, rather than the intensities, of the lines. In all published spectroscopic investigations²⁻⁸ of the fundamental absorption region of HCl, the measurements have been obtained for a single long gas-column. The unpublished thesis of Brinsmade and the recent indirect evidence adduced by Kemble⁹ indicate the possibility that the exponential law is inapplicable to the observed measurements. This conclusion is directly confirmed by the experiments reported in this paper. Hence it is not possible to estimate either the absorption coefficient for a particular frequency or the integrated value of the coefficient from data on a single tube-length.

For the case of the simple vibration-rotation bands under which the fundamental band of HCl is to be classified the following theoretical formula has recently been proposed by Kemble⁹

$$\alpha_M = (c/\nu^3) \bar{p}_M e^{-W_M/kT} \quad (2)$$

where ν is the frequency associated with the transition giving rise to the line, the exponential factor is the Boltzman factor taken for the initial state and \bar{p}_M denotes the arithmetic mean of the a priori probabilities involved in the transition. Kemble's derivation of Eq. (2) is based on a splitting up of the stationary states of the molecule by a hypothetical weak magnetic field and the assumption that the sum of the intensities of the simple Zeeman components passes continuously into the intensity of the band line as the strength of the magnetic field approaches zero.

The measurements of the intensities of lines in atomic spectra have suggested the empirical, so-called "summation rule."¹⁰ The rule has since

² Burmeister, *Verh. d. D. Phys. Ges.* **15**, 589 (1913).

³ E. S. Imes, *Astrophys. J.* **1**, 251 (1919).

⁴ J. Brinsmade and E. C. Kemble, *Proc. Nat. Acad. Sci.* **3**, 420 (1917).

⁵ E. von Bahr, *Verh. d. D. Phys. Ges.* **21**, 115 (1913).

⁶ Colby and Meyers, *Astrophys. J.* **53**, 300 (1921).

⁷ Colby, Meyers and Bronk, *Astrophys. J.* **57**, 7 (1923). (The last two papers give only the positions of the absorption maxima and not the entire absorption curve.)

⁸ G. Becker, *Zeits. f. Physik* **34**, 255 (1925).

⁹ E. C. Kemble, *Phys. Rev.* **25**, 1 (1925).

¹⁰ N. Burger and H. B. Dorgelo, *Zeits. f. Physik* **23**, 258 (1924).

been justified on theoretical grounds.^{11,12} Its extension to band spectra leads to an expression of the same general form as Eq. (2) except that the form of the frequency factor is left undetermined. Also the analogue, on the basis of the summation rule, of the probability factor in Eq. (2) takes on a different set of values for an arbitrary choice of statistical weights from that taken on by the term occurring in Eq. (2).

The new quantum theory introduced by Heisenberg and Born suggests that the intensity of the Zeeman component correlated with the transition $m \rightarrow m \pm 1$ and $r \rightarrow r \pm 1$, where m and r are the rotational and spatial quantum numbers respectively, is proportional^{13,14} to $(m \pm r)(m \pm r - 1)/(m^2 - \frac{1}{4})$. The intensity for the transition $m \rightarrow m \pm 1$, $r \rightarrow r$ varies as $(m^2 - r^2)/(m^2 - \frac{1}{4})$. It may be shown that a summation over all allowed values of r and application of the Kemble, Heisenberg postulate of the continuity of intensities^{9,11} leads to a linear dependence on the rotational quantum number in harmony with (2).

The experimental verification of Eq. (2) and the resolution of the ambiguity^{9,12,15} as regards the exact variation of the probability factor (and therefore the proper choice of weight factors) are important consequences of the present work.

The procedure adopted for evaluating the integrated absorption coefficients consisted in obtaining the absorption curves for six different absorbing columns varying in length from 0.0988 cm to 2.97 cm. Curves were drawn of the areas under the absorption lines plotted against tube-length. The gas columns were sufficiently short to permit of reasonably accurate extrapolation of these curves to zero tube-length. The initial slopes of these extrapolated curves, as will appear later, yield the desired absolute integrated absorption coefficients.

EXPERIMENTAL WORK

The HCl gas was obtained by dropping concentrated sulphuric acid on constant boiling HCl solution. Five Emmerling absorption towers were used to purify the gas and every precaution was taken to avoid its contamination.

The infra-red spectrometer was the quartz prism instrument constructed by Brinsmade and used by Brinsmade and Kemble. A variety of modifications in the details of the apparatus gave increased sensitivity and steadiness. It was of the Wadsworth¹⁶ constant deviation type as modified by Gorton.¹⁷ Fig. 1 shows a diagram of the optical system. The instrument

¹¹ W. Heisenberg, *Zeits. f. Physik* **31**, 617 (1925).

¹² R. H. Fowler, *Phil. Mag.* **50**, 1079 (1925).

¹³ D. M. Dennison, *Phys. Rev.* **28**, 318 (1926).

¹⁴ I. Tamm, *Zeits. f. Physik* **37**, 685 (1926). Dr. Tamm seems to infer incorrectly that neglecting the Boltzman factor the band intensities are practically independent of the rotational quantum numbers and follow the Maxwell-Boltzman distribution law.

¹⁵ G. H. Dieke, *Zeits. f. Physik* **33**, 161 (1925).

¹⁶ Wadsworth, *Phil. Mag.* **38**, 137 (1894).

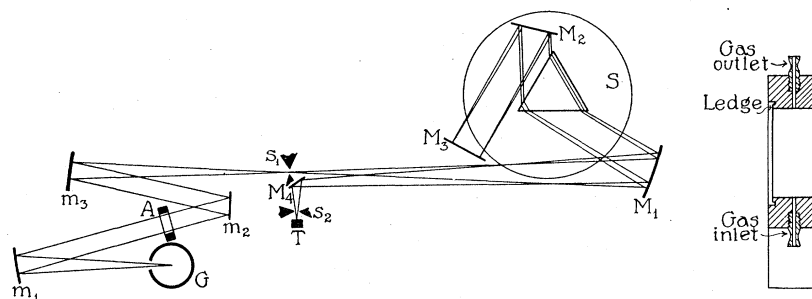
¹⁷ Gorton, *Phys. Rev.* **7**, 66 (1916).

was provided with a 60° quartz prism having faces 5.1 cm high and 4.3 cm wide. The focal length of the concave mirror M_1 was 50 cm. The extreme spectral range falling on the thermopile slit was computed to be 126A, with both slit widths set at 0.3 mm.

The receiving instrument was a twenty junction bismuth silver vacuum thermopile constructed by Coblenz. Every effort was made to rid the thermopile case of occluded gas by long continued pumping.

The galvanometer was a Weston gravity controlled d'Arsonval type of instrument. The sensitivity was usually adjusted to a value between 2×10^{-8} and 8×10^{-9} volts per mm at a meter's scale distance.

A Nernst glower actuated by a steady alternating current was used as a light source. Direct current from storage batteries was used to run a



Figs. 1 and 2. Optical plan of set-up. G , Nernst glower; m_1 and m_3 , concave mirrors; m_2 , M_3 , M_4 , fixed plane mirrors; M_2 , plane rotating mirror; M_1 , collimating mirror; s_1 , entrance slit; s_2 , thermopile slit; T , thermopile; A , absorption chamber.

high-frequency motor-generator loaned to the writer by Professor G. W. Pierce. The usual variation in mean square current over a period of three or four hours was less than 0.005 amp.

The first absorption tube consisted of two brass frames between which cylinders of various lengths could be fitted. All the absorption tubes were fitted with quartz windows about 2 mm thick. The three shortest tubes (Fig. 2) were specially designed to permit an accurate measurement of the length of the absorbing column. The tubes were made of brass and an annular depression was cut around each window ledge. The windows were sealed in place by means of a ring of de Khotinsky cement placed on this depression. By this method it was possible to keep the window ledges perfectly clean so that the length of the tube could be measured by micrometering the distance between the ledges with the quartz plates removed.

The necessary data were (1) the transmission, T_1 , of the tube itself free from gas, and (2) the transmission, T_B , of the gas-filled tube. In terms of these transmissions the gas absorption is

$$1 - T_1/T_B \quad (3)$$

The tube transmission will be referred to as the "base-line," the precise determination of which presented a rather difficult problem. A difference

of the order of 0.5 percent was found for the variation in transmission of a 65 cm tube when filled with room air and when evacuated. Therefore, for the tube-lengths used in this research, the transmission of the air-filled tube could be used as the base-line. The stumbling block was the removal of all trace of gas from the absorption chamber since merely blowing or sucking air through was ineffective.

Four distinct methods of obtaining data to fix the base-line were followed and will be distinguished by the letters (a), (b), (c) and (d). For the 0.96 cm and 2.97 cm tubes, the procedure (a) was the following: Preliminary to the first run on either tube the two window frames, with the windows already attached, were mounted a distance apart equal to their separation with the particular brass cylinder to be used in the run and about eight base points were obtained in the region to be covered. The windows were purposely not treated to remove adsorbed gas since it was essential that the condition of the surfaces be the same as when the cylinder was in place and the tube filled with gas. This adsorption was quite apparent for, even after the exposure of the quartz windows to the air for a half-day, slight warming was sufficient to liberate enough gas to give off the sharp characteristic odor of HCl. The base-line having been determined, the glower the mirror and the stops which secured proper alignment were not varied till the run had been completed. The whole band could generally be covered in two runs (or three runs at most), therefore, for the second run the base-points were determined at the end of the run. This method of fixing the base-curve solved the problem of minimizing the inaccuracies due to the presence of occluded gas on the windows.

Method (a) was inapplicable to the shorter tubes which were constructed of a single brass plate. For two of the four runs on the 0.169 cm tube, the base-line was determined before and checked after the run, by evacuating the tube. This was method (b). For the other two runs and for the runs on the 0.248 cm tube and the run on the 0.0988 cm tube covering the negative branch, the procedure (c) was to determine the base-points for the positions of minimum absorption as these low absorption points were reached during the course of the experiment, a large capacity piston pump being used to take out most of the gas and the exhaustion then improved by cutting out this pumping unit and replacing it with a Cenco "Hyvac" oil pump. This method reduced the inaccuracies introduced by progressive variations during the course of the run and in the event of some sudden change limited the possibility of error to one line instead of casting suspicion on all the values of the run. In the case of the run on the positive branch with the 0.0988 cm tube, readings were taken at each point with the tube alternately evacuated and filled with gas. In this method (d) the tube was not moved at all and the true transmission was immediately given as the ratio of the successive readings when the tube was filled with gas and when it was pumped down. If the gas could be completely removed in a conveniently short time this method would be the most satisfactory inasmuch as it eliminates the intermediate step of obtaining the values of the glower

emission. The method is most successful when the volume to be evacuated is a minimum, which explains its use for the shortest tube-length. Because of possible unforeseen complications in the way of window-adsorption effects, it seemed advisable to limit the use of this plan to the one tube-length and test its value by the plausibility of the results obtained as compared with those for the other tube-lengths.

The spectrometer settings were read on a revolution counter and dial. In general, the interval used was about one dial revolution (the absorption peaks were about six turns apart near the center of the band) except in the neighborhood of the maxima where sometimes quarter revolutions were used.

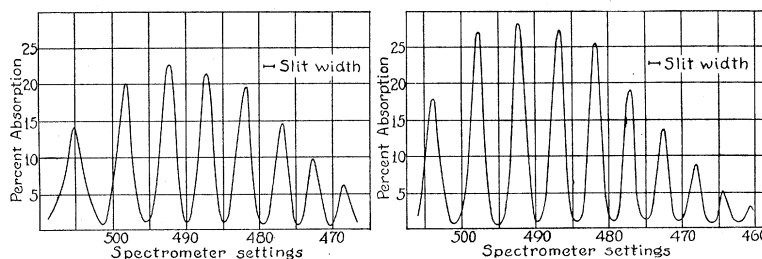
In calculating the absorption from the experimentally determined diminution in light intensity, it was assumed that the effects of selective scattering and selective reflection at the quartz-gas interface were negligible. As the curves of total absorption (area under peak) plotted as a function of the tube-length extrapolate naturally to the value zero for zero tube-length, it hardly seems possible that there could have been any appreciable selective reflection. The writer has no definite check on the assumption that scattering may be neglected, but since the selective scattering should be proportional to the absorption it is not likely that it could effect, markedly, the apparent relative absorption intensities of the different lines.

THEORY OF THE CALCULATIONS

The general plan for obtaining the integrated absorption coefficients has already been suggested in the introduction and it has been pointed out that the procedure involved the determination of the area under each absorption line for several tube-lengths. On denoting these areas, when measured in frequency units, by the symbol $A_M(x)$ it is possible to write

$$A_M(x) = \int_M [(T_B - T(x))/T_B] d\nu \quad (4)$$

where T_B is the base-line transmission and $T(x)$ is the transmission of the gas-filled tube of length x . Strictly speaking the absorption curve for a



Figs. 3A and 3B. Characteristic absorption curves taken with 0.169 cm and 0.248 cm tubes. R branch.

given line extends from $\nu=0$ to $\nu=\infty$ but the estimates were made on the assumption that the true area was closely approximated by the area under

the experimental curves, uncorrected for slit width, included between two successive minima separating the line in question from its neighbors (cf Figs. 3A and 3B).

With regard to the neglect of the overlapping of adjacent lines, it may be pointed out that (a) adjacent lines do not differ greatly in intensity and the overlapping of lines of equal intensity clearly leads to no error, (b) in the region where the intensities might be considered as changing comparatively rapidly the net gain from the more intense neighbor is, in general, very nearly balanced by the net loss to the less intense adjacent line, and (c) for the very short tube-lengths employed in these experiments, the intensity in the region between absorption lines is quite small.

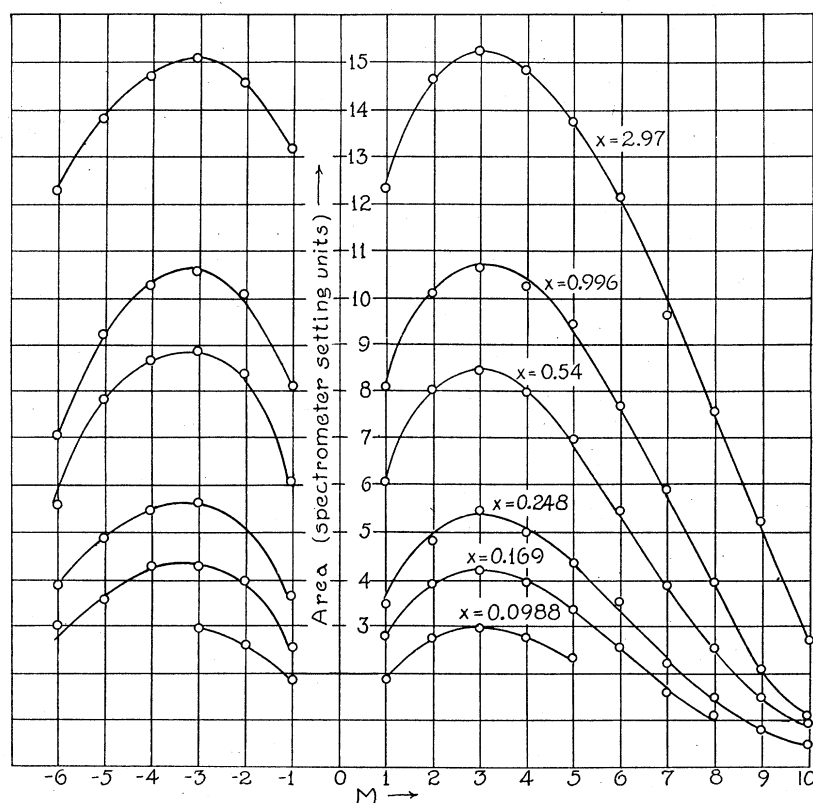


Fig. 3C. Smoothing curves.

The areas under the various absorption maxima were measured from the original curves without correcting for slit width. Clearly, since the area under any line regardless of slit width gives the fractional amount of light abstracted from a beam whose intensity is independent of frequency, the areas should not be affected by variations in the slit width which do not lead to serious overlapping.

For estimating the areas under the absorption curves large scale plots similar to Figs. 3A and 3B were used. A sufficient number of points were available for the lines, usually about seven or eight at least, to indicate the general appearance though, of course, there was some latitude in defining their shapes. For most of the tube-lengths several sets of overlapping data were available and the absorption data used in the calculations are the averages of these for each tube-length.

In the adaptation of the measured areas to the calculations a preliminary smoothing process was resorted to in order to reduce the inaccuracy in the individual lines. The smoothing was effected by drawing the best curve through the correlated points in a plot of line-number against line-area (Fig. 3C). In all the calculations based on direct application of the "five-term polynomial" method and in all methods involving use of the data for the line $M=3$ a second smoothing occurred in the choice of the most plausible curve through the points in the plots of area against tube-length of which Fig. 4 is the type.

TABLE I
Smoothed areas in frequency units.

M	2.97 cm	.996 cm	.54 cm	.248 cm	.169 cm	.0988 cm
1	1.178	.767	.574	.346	.265	.175
2	1.423	.979	.777	.484	.379	.262
3	1.526	1.071		.536	.415	.292
4	1.536	1.063	.826	.526	.401	.284
5	1.405	.986	.726	.455	.348	.236
6	1.317	.825	.581	.359	.270	
7	1.078	.643	.424	.257	.186	
8	.848	.433	.284	.166	.108	
9	.605	.287	.167	.088		
10	.329	.124	.103	.0509		
-1	1.172	.737	.559	.328	.238	.166
-2	1.285	.884	.731	.449	.345	.232
-3	1.285	.900	.754	.478	.374	.253
-4	1.225	.853	.717	.454	.345	
-5	1.103	.744	.623	.393	.292	
-6	.956	.551	.470	.300	.210	

The original areas were in units of percent and spectrometer settings. To change to a frequency standard two independent methods were employed to estimate $\Delta\nu/\Delta\theta$ where θ refers to the dial settings and ν to the frequency. In the first method this ratio was calculated from the prism-angle and the known dispersion curve of quartz. In the second method the values of $\Delta\theta$ for successive absorption maxima as determined from the experimental plots similar to Figs. 3A and 3B and the corresponding values of $\Delta\nu$ as given by Colby and Meyers,⁶ were plotted against line number M . The ratios of the values of the ordinates of the two curves for any value of M is the correlated value of $\Delta\nu/\Delta\theta$. The agreement of the two sets of values was quite good for the positive branch, although there was a slight departure for the negative branch. The mean of the two estimates was used in the calculation.

The primary purpose of the experiments was to determine the values of α_M for the various lines. It may immediately be shown that if we plot the area under an absorption line as a function of the tube-length x , α_M should be the slope of the curve at $x=0$. Thus, from the fundamental relation between the absorption coefficient and the intensity $I(\nu)$

$$dI(\nu) = -\mu(\nu)I(\nu)d\nu \quad (5)$$

we obtain

$$A_M(x) = \int_M (1 - e^{-\mu(\nu)x})d\nu \quad (6)$$

which gives immediately

$$(dA_M/dx)_{x=0} = \alpha_M = \int_M \mu(\nu)d\nu \quad (7)$$

The evaluation of the initial slopes of the various graphs of area against tube-length required by Eq. (6) is somewhat complicated by the large curvature near the origin. Several methods of attack were employed in the attempt to get as accurate a solution of the problem as possible.

The first of these methods consisted in fitting the five-term polynomial formula

$$A_M(x) = \omega^{(1)}x + \omega^{(2)}x^2 + \dots + \omega^{(5)}x^5 \quad (8)$$

to the data. This method is inaccurate since it accentuates the influence of the shorter tube-lengths in that a very small error in the area for the shortest tube produces a large error in the calculated value of $\omega^{(1)}$ or α_M .

A method which eliminates this difficulty is most easily explained if we start from the crude assumption that the absorption coefficient curves ($\mu(\nu)$ plotted against ν) for the various lines have the same shape so that by suitable change in the scale of ordinates any curve could be superposed on any other. This assumption is expressed by

$$\mu_M(\nu) = K_M F[\nu - (\nu_0)_M] \quad (9)$$

where $(\nu_0)_M$ is the frequency of the center of the M th line. If it were true, $A_M(x)$ would be a function of the product $K_M x$ or, what comes to the same thing, of $\alpha_M x$. Then if we consider two points corresponding to the same ordinate A on curves for different lines, this product must be the same for both. In other words for two such points

$$x_{M'}/x_M = \alpha_M/\alpha_{M'} \quad (10)$$

Hence the ratio of the integrated absorption coefficients for any two values of M could be determined by plotting curves of area against tube-length like the one of Fig. 4, and comparing the abscissas of any two points with equal ordinates.

This method of procedure leads, in practice, to values of $\alpha_M/\alpha_{M'}$, which vary with the ordinate (area) for which they are calculated, showing that

the lines are not exactly the same in shape. This is to be expected since HCl is a mixture of the constituents HCl_{35} and HCl_{37} so that each absorption line is an isotopic doublet. The separation of the doublet components depends on the rotational quantum numbers¹⁸ and therefore varies with M .

The variation of $x_{M'}/x_M$ with the corresponding ordinate A is not rapid for small values of A , however, and since

$$\lim_{A \rightarrow 0} \frac{x_{M'}}{x_M} = \lim_{x_M \rightarrow 0} \frac{x_{M'}}{x_M} = \frac{\alpha_M}{\alpha_{M'}} \quad (10.1)$$

it follows that the extrapolation of the $x_{M'}/x_M$ values to zero A (or zero x_M) gives an accurate method of evaluating the *relative* absorption coefficients.

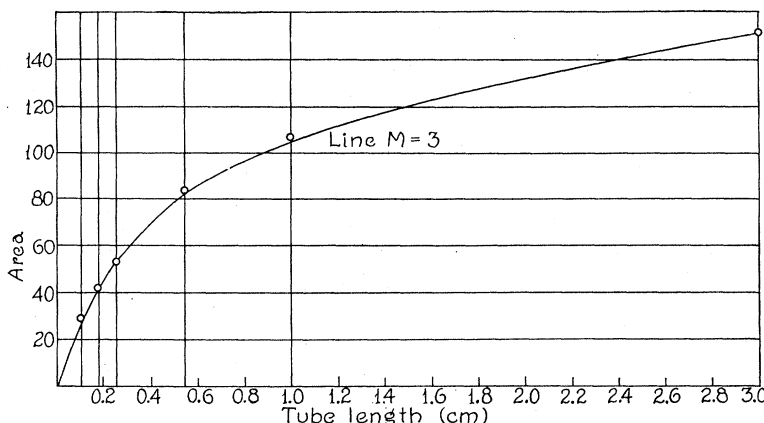


Fig. 4. Curve showing the variation of line area with tube-length.

In applying this method the line $M = 3$ was arbitrarily selected as a standard of comparison and an accurate curve was drawn through the points defined by corresponding values of smoothed area and tube-length (Fig. 4). For any other absorption line M each area obtained from a run using a gas column of length x_M was used to determine a value x_3 for which the ordinate of the standard curve was equal to the area in question. Then the values of the ratio x_3/x_M were plotted against x_M for each absorption line. These lines would have been straight lines, with ordinates equal to the relative absorption coefficients desired, if the shapes of all the lines had been the same. It is evident from Fig. 5 that the extrapolation to the axis of ordinates is a fairly safe one.

In view of the appreciable experimental errors, it is desirable to have some theoretical guide for drawing "best curves" for x_3/x_M . Such a guide will be suggested by the following analysis. The absorption coefficient may be written

$$\mu(\nu) = \mu'(\nu - \nu_1) + \mu''(\nu - \nu_2) \quad (11)$$

¹⁸ R. S. Mulliken, Phys. Rev. 25, 119 (1925).

where $\mu'(\nu - \nu_1)$ and $\mu''(\nu - \nu_2)$ are the respective contributions of each isotope and ν_1 and ν_2 are the frequencies of the absorption maxima for the corresponding isotopes. It will be brought out that the form of the absorption curves is determined by the magnitude of the terms

$$\int_M \mu(\nu)^n d\nu = \int_0^\infty \{ \mu'(\nu - \nu_1) + \mu''(\nu - \nu_2) \}^n d\nu \quad (11.1)$$

The expansion of $A_M(x)$ leads to the series

$$A_M(x) = \mu_M^{(1)} x - \mu_M^{(2)} x^2/2! + \mu_M^{(3)} x^3/3! \dots \quad (12)$$

where

$$\mu_M^{(j)} = \int_M [\mu_M(\nu)]^j d\nu$$

Let us make the assumption expressed in Eq. (9), then substituting $x' = xK_M/K_3$ in Eq. (12) gives for the expansion of A_M in terms of x'

$$A_M(x') = \mu_M^{(1)} K_3 x' / K_M - \mu_M^{(2)} \{ K_3 x' \}^2 / K_M^2 2! + \mu_M^{(3)} \{ K_3 x' \}^3 / K_M^3 3! \quad (12.1)$$

If the assumption made about the factorization of the absorption coefficient into a term dependent on the quantum numbers and another independent of the line were true (vide Eq. 9) it is seen that the coefficients of the various powers of the primed variables in Eq. (12.1) would be identical with those in the expression of $A_3(x)$ in powers of x . Actually, from the fact that $\partial[\mu'(\nu - \nu_1)]/\partial\nu$ (or $\partial[\mu''(\nu - \nu_2)]/\partial\nu$) is of one sign from 0 to ν_1 (or ν_2) and from ν_1 (or ν_2) to ∞ and the knowledge that $\mu'(\nu - \nu_1)$, $\mu''(\nu - \nu_2) > 0$ it may be shown analytically or made evident graphically, that the integral $\int_0^\infty [\mu(\nu)]^n d\nu$ for $n > 1$ steadily diminishes on increase of the isotope separation. An equivalent statement is that for lines for which $(\Delta\nu)_M > (\Delta\nu)_3$, where $\Delta\nu$ is the isotope separation, the following inequality holds

$$\mu_M^{(j)} \{ K_3 / K_M \}^j < \mu_3^j \quad (9.1)$$

The sign of the inequality is reversed if $(\Delta\nu)_3 > (\Delta\nu)_M$.

(12) Inverting the series gives

$$x = a_M^{(1)} A_M + a_M^{(2)} A_M^2 + \dots + a_M^{(i)} A_M^i + \dots \quad (12.2)$$

Eq. (12.2) may be employed to yield the rigorous value of the ratio x_3/x_M . Thus

$$x_3/x_M = \frac{a_3^{(1)} A + a_3^{(2)} A^2 + \dots}{a_M^{(1)} A + a_M^{(2)} A^2 + \dots}$$

where x_3 and x_M are the values of x correlated with a given value of $A(x)$ (the subscript M or 3 would have no significance here) for the line $M=3$ and for the M th line respectively. Expanding the ratio in powers of A and then replacing A by its expansion in terms of x_3 or x_M yields

$$\begin{aligned}
 x_3/x_M &= \frac{a_3^{(1)}}{a_M^{(1)}} \left\{ 1 + \mu_3^{(1)} x_3 \left(\frac{a_3^{(2)}}{a_3^{(1)}} - \frac{a_M^{(2)}}{a_M^{(1)}} \right) + (\{\mu_3^{(1)}\}^2 - \mu_3^{(2)}) x_3^2 \right. \\
 &\quad \left[\left\{ \frac{a_3^{(3)}}{a_3^{(1)}} - \frac{a_M^{(3)}}{a_M^{(1)}} \right\} - \frac{a_M^{(2)}}{a_M^{(1)}} (\quad) \right] + \dots \\
 &= \frac{a_3^{(1)}}{a_M^{(1)}} \left\{ 1 + \mu_M^{(1)} x_M \left(\frac{a_3^{(2)}}{a_3^{(1)}} - \frac{a_M^{(2)}}{a_M^{(1)}} \right) + (\{\mu_M^{(1)}\}^2 - \mu_M^{(2)}) x_M^2 \right. \\
 &\quad \left. \left[\{ \dots \} - \frac{a_M^{(2)}}{a_M^{(1)}} (\quad) \right] + \dots \right.
 \end{aligned}$$

where the $\mu_3^{(i)}$, $\mu_M^{(i)}$ coefficients occur in Eq. (12) and it is evident that

$$\lim_{x_M \rightarrow 0} x_3/x_M = \lim_{x_B \rightarrow 0} x_3/x_M = a_3^{(1)}/a_M^{(1)} = \mu_M^{(1)}/\mu_3^{(1)}$$

The coefficients $a_3^{(i)}$ and $a_M^{(i)}$ of the inverted series (12.2) are such functions of $\{\mu_M^{(i)}\}$ that if the distinction were dropped between $\{\mu_M^{(i)}\}^i$ and $\mu_M^{(i)}$ the ratio $a_M^{(i)}/a_M^{(1)}$ would reduce to unity. (For instance $a_M^{(1)} = 1/\mu_M^{(1)}$, $a_M^{(2)} = -\mu_M^{(2)}/\{\mu_M^{(1)}\}^3$).

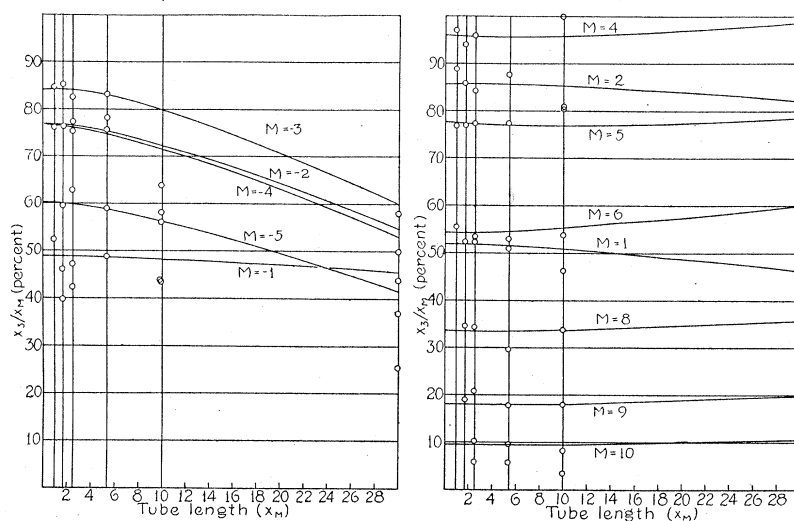


Fig. 5. Extrapolation plots for the "ratio" method.

It is, therefore, easily understood that the assumption of Eq. (9) would lead to the equality of the ratios $a_M^{(i)}/a_M^{(1)}$ and $a_3^{(i)}/a_3^{(1)}$ and this would carry with it the vanishing of all the terms in powers of the variable in Eq. (13). The isotope doubling disturbs the equality of $a_M^{(i)}/a_M^{(1)}$ and $a_3^{(i)}/a_3^{(1)}$ and the inequality of Eq. (9.1) points to the conclusion that the x_3/x_M vs x_M curves should be concave upwards for $3 < M$ and concave downward for $M < 3$, (at least initially.)

Although the rotational isotope separation is essentially a quadratic function of the quantum numbers, the resultant of the vibrational and rotational isotope separations may be considered as varying very nearly linearly in the region of the band center. Bearing this in mind, it is clear that since the values of A for the lines $M=7, 8, 9, 10$ were quite small for all the tube-lengths used the influence of the higher order terms in Eq. (13) would not be expected to be pronounced, but in the case of the negative branch where the areas are larger for lines equally far removed from the line $M=3$, the curvature should be more noticeable.

To determine the value of x_3 correlated with a given area, it was necessary to approximate the curve of area against tube-length for the line $M=3$ with some care. Two methods in particular were used for this purpose. One of these is discussed in some detail under the heading of Method III; the other, which will be referred to as Method II, utilized formula (8) to locate points corresponding to tube-lengths 0.01 cm, 0.02 cm, etc.

TABLE II
Interpolated values of areas.

Method II		Method III		Method IV	
x_3 (cm)	$A(x)/12.28$ $\times 10^{-12}$	x_3 (cm)	$A(x)/12.28$ $\times 10^{-12}$	x_3 (cm)	$A(x)/12.28$ $\times 10^{-12}$
0.01	0.3697	0.0323	1.103	0.01	0.37
0.02	0.716	0.0645	2.001	0.1	2.9
				0.2	4.67
0.04	1.346	0.129	3.42		
0.08	2.276	0.323	6.25		
		0.645	8.95	1.0	1.065
		1.29	12.2	2.0	13.5

Method III proceeds as follows: since the value of $\int_M(1 - \exp(-\mu(\nu)x))d\nu$ is only slightly affected by changes in the functional form of $\mu(\nu)$, whose influence is perceptible only when the integrand is quite small, one is prompted to use as a simple approximation

$$\mu(\nu) = \frac{a_M}{(\nu - \nu_1)^2 + b_M^2} \quad (14)$$

where a_M and b_M are certain characteristic constants. Therefore

$$A_M(x) = \int_{-\infty}^{+\infty} (1 - e^{-a_M x / (\nu^2 + b_M^2)}) d\nu$$

On defining n and Z as $a_M x / b_M^2$ and ν / b_M respectively, the last integral may be exhibited as

$$A_M(n) = 2b_M \left\{ \int_0^c (1 - e^{-n/(Z^2+1)}) dZ + \int_c^\infty (1 - e^{-n/(Z^2+1)}) dZ \right\}$$

The transformation $y=1/Z$ applied to the second integral of the above makes it possible to write

$$A_M(n) = 2b_M \left\{ \int_0^\infty (1 - e^{-n/(z^2+1)}) dz + \int_{1/c}^0 (1 - e^{-y^2 n/(y^2+1)}) dy / y^2 \right\} \quad (15)$$

The integrals were evaluated graphically by finding the areas under the integrand curves for $n = 0.5, 1, 2, 5, 10, 25$. The constant c was taken as 20 (so that an approximation which replaced the second integral by n/c would have been only one percent out of the way).

The resulting plot of A_M against n was very similar to the curve of area as a function of tube-length except for the matter of scale. It was not difficult to apply a process of trial and error to establish values of n and b which secured a good fit of the theoretical A, n curve and the experimental A, x curve. The procedure consisted in studying the ratios of the two ordinates of the A, x curve, for ratios of the x 's equal to that between an arbitrary pair of n values and noting when this ordinate ratio was equal to the corresponding ordinate ratio of the A, n curve.

The constants $a_3 = 1.67 \times 10^{21}$ and $b_3 = 1.04 \times 10^{10}$ were evaluated from the relations $2b_3 = A_3(x)/A_3(n)$ and $a_3 = b_3^2 n/x_3$. The integrated absorption coefficient for the line $M = 3$ is

$$\alpha_3 = \int \mu_3(\nu - \nu_0) d\nu = \pi a_3 / b_3 \quad (16)$$

This is the only absolute absorption coefficient calculated in this way. The deviation of the extrapolation curve obtained by this method from that suggested by the terminated power series expansion method (Method II) was slight and in the expected¹⁹ direction in that the slope at the origin of the former curve was the greater.²⁰

RELIABILITY OF THE RESULTS

The principal sources of inaccuracy in the results given in this paper arise from: (a) experimental uncertainty in taking readings; (b) errors in the base-lines; (c) the cumulative effect of errors which separately may be very small (i.e. use of an inaccurate effective tube-length for the calculations, non-uniformity of the Nernst glower emissivity, uncertainty regarding $\Delta\nu/\Delta\theta$, errors in plotting the data and measuring the areas, etc.); (d) uncertainty regarding the possible effect of selective reflection at the windows of the chamber; (e) errors inherent in the methods employed for calculating the integrated absorption coefficients.

A consideration of the average number of readings and the accuracy of each makes it plausible to assume an accuracy of 0.75 percent for points of the base-line and transmission curves. For gauging the effect of an error of this magnitude on the precision of the measured line areas, it is suggestive

¹⁹ Since the alternating power series was terminated at a positive term and therefore would be expected to give too high values of ω^1 .

²⁰ A fourth method of calculation depended on the assumption of a step like variation for $\mu(\nu)$. The analysis is somewhat involved and is therefore omitted although the value of α_3 calculated in this way is included in Table II.

to treat the absorption line as being of a triangular shape and height k . Considering T_B to be sensibly constant over the line allows us to write

$$\frac{\delta A_M}{A_M} = \frac{\delta T_B}{T_B} \left\{ \frac{T_B}{T_B - k} \right\} \quad (17)$$

which reduces to (constant) $\times \delta T_B/T_B$ when it is realized that k/T_B is independent of T_B . Similarly the effect of inaccuracy in the transmission curve may be written

$$\delta A_M/A_M = \delta T^{(x)} / [T^{(x)} - k] \quad (17.1)$$

These formulas show the importance of using as high values for the base-line transmission as possible. On applying the Fresnel formula for the unavoidable reflection loss at each of the four reflecting surfaces of the two quartz windows, it turns out that in this work the value of the base-line transmission actually attained was only two percent or three percent less than that theoretically possible for infinitely thin windows.

The applications of expressions (17) and (17.1) suggest errors of the order of magnitude of 1 to 8 percent, the lesser values being correlated with the more intense lines in the R branch and the higher values with the weaker lines in this branch and the farther lines in the P branch.

One gauge of the effect due to the non-systematic causes enumerated under (c) would be the difference between the original and the smoothed areas as indicated in Fig. 3C. The smoothing curves are, however, somewhat arbitrary and the fact that the differences are very slight is not to be accepted too easily as a proof of the reliability of the results. However, it is not probable that the error is over 3 or 4 percent for the more accurate lines to 8 or 9 percent in the case of poorer measurements—the correlation being the same as for errors of type (b). The relative values are probably more accurate.

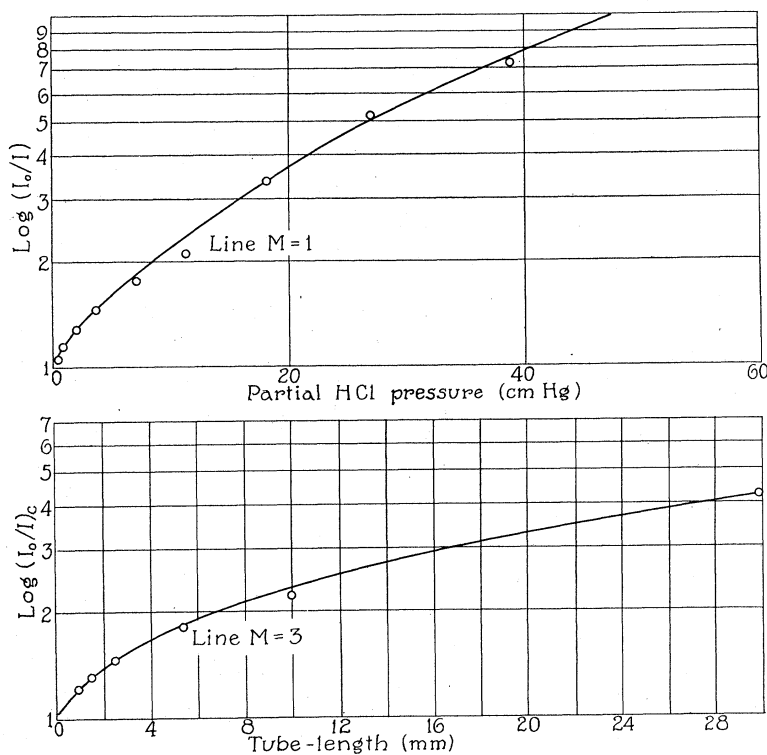
In using Method I an analysis of the error introduced in the final absolute values of the absorption coefficients by the estimated inaccuracies in the areas, indicates that the precision limits are about 15 percent for the stronger lines in the positive branch to about 25 percent for the weaker lines and the lines in the negative branch. The ratio methods are much more reliable especially for the relative values. It appears that a fair estimate for these methods would fix the reliability as being about 10 to 20 percent.

Both the mean square deviation of the calculated points from the best curves in Figs. 3A and 3B and the apparent close check between theory and experiment, to be pointed out later, suggests that the actual accuracy attained is better than these estimates would indicate. The close agreement in the estimates of the absolute value of α_3 as obtained from the four methods of calculating described above lends weight to the reliability of the values of α_M given in Table III.

DISCUSSION OF RESULTS

Before entering upon a study of the application of the experimental values of the integrated absorption coefficients to the primary theoretical problem of absorption intensities, it is worth while to remark some important general consequences of the data obtained in this research.

Width of spectral lines and failure of exponential law. One of the striking results is the unexpected magnitude of the absorption for short gas columns as compared with that to be expected from the application of the exponential law to the data for long tube-lengths. The failure of the exponential law for the line $M=3$ is shown by Fig. 6A. The ordinates are the quantities $\log_{10} (I_0/I)_c$ where $(I)_c$ is the apparent intensity of the transmitted light after correction for slit width by the Paschen-Runge²¹ formula and the tube-lengths are the abscissas. If the exponential law were obeyed the points in Fig. 6A would lie on a straight line through the point $\log (I_0/I) = 1, x = 0$. The decided curvature is proof that the exponential law is not valid in the region of maximum absorption.



Figs. 6A and 6B. Test of exponential law.

The law fails also when the partial pressure is varied instead of the tube-length, as indicated in Fig. 6B. No slit width correction was applied for

²¹ F. Paschen, Ann. d. Physik 60, 661 (1897).

this case but it is fairly clear that such a small correction would not affect the conclusion.

The apparent failure of the exponential law is due, no doubt, to the fact that the resolving power of the spectrometer with the slit widths used was not sufficient to give the true shape of the absorption curve even when the slit width correction is applied.

The lines are narrower and 'deeper' than they seem. In fact, we can calculate the equivalent half-breadth of the line $M = 3$ from the approximating function used in Method III. From Eq. (14) it is readily seen that the half-breadth is $2b_3$. The numerical value is about²² 2.1×10^{10} frequency units. This is quite small in comparison with the spacing of the lines, which is about 54×10^{10} frequency units in the neighborhood of the line $M = 3$. This is the half-breadth of a single line having the same A, x curves as the actual line $M = 3$. Since the theoretical separation of the isotopic components is 6.78×10^{10} frequency units, it is clear that the actual half-breadth of the individual components, as calculated by this method, must be less than the equivalent half-breadth of the pair. Moreover, the variation in the isotopic separation with M should have a noticeable effect on the shape of the A, x graphs, as is proved by the curvature of the ratio plots of Figs. 3A and B.

The half-breadth given above is about one-fourth of the lower limit assigned by G. Becker⁸ on the basis of his study of the effect of pressure on the HCl band, and about one-fifth of the estimate given by Tolman.²³

The nature of the absorption curves may be interpreted as follows: Since the absorption lines appear to be really very sharp and quite intense at the center, most of the initial absorption is due to the center of the line and in the case of the strong lines, radiation of frequency corresponding to peak absorption is almost completely absorbed in less than one cm of gas path. For the long tubes the increase in absorption with tube-length is from the less intense absorbing region on either side of the maximum.

The relative intensities of the lines. An immediate conclusion to be drawn from the tabulated values of the integrated absorption coefficients (Table III) is that the intensities in the positive branch are higher than those in the negative branch as required by Eq. (2). Although the single published absorption curve of Brinsmade and Kemble is in agreement with this result the most frequently quoted experimental data (i.e. those of Imes) seemed to belie this prediction of theory.²⁴

²² This estimate depends somewhat on the line shape assumed. A subsequent paper will consider the effect, on the calculated values, of modifications in the supposed line shape and will give the results for the isotopic doublet structure.

²³ R. Tolman, Phys. Rev. **23**, 693 (1924).

²⁴ Not only are corresponding maxima of Imes' absorption curves distinctly higher for the lines in the negative branch but the intensity estimates derived from these curves by Tolman²³ also emphasize the negative branch. The fact that $\Delta\nu/\Delta\theta$, for a grating decreases with ν indicates one explanation for the appearance of Imes' curves.

Fig. 7 shows a comparison of the experimental results with the formula of Eq. (2). The theoretical points yielded by the two sets of weights $p_M=1, 3, 5, 7, \dots$, and $p_M=2, 4, 6, \dots$, are both indicated. For the

TABLE III

Tabulated values of the integrated absorption coefficients.

M	Method I $\alpha_M=46.6 \times 10^{10}$	α_M/α_3 Ratio Methods	Method III 50.2×10^{10}	Method IV 51.6×10^{10}
	Method I α_M/α_3		α_M/α_3 Theoretical Values ($p_i=1,3,5$)	α_M/α_3 Best Values ($p_i=2,4,6$)
1	0.552	0.518	0.474	0.606
2	0.883	0.857	0.853	0.895
3		1.00	1.00	1.00
4	0.976	0.959	0.961	0.926
5	0.829	0.774	0.782	0.737
6	0.537	0.542	0.555	0.515
7	0.310	0.333	0.345	0.316
8	0.192	0.185	0.189	0.172
9	0.0847	0.091	0.092	0.083
10	0.081	0.047	0.040	0.036
-1	0.479	0.486	0.444	0.570
-2	0.781	0.764	0.736	0.789
-3	0.877	0.841	0.840	0.840
-4	0.79	0.768	0.736	0.731
-5	0.66	0.604	0.584	0.550
-6	0.51	0.347	0.389	0.333

latter sequence only the points calculated from Kemble's theory are plotted since obviously the experimental intensity variations are non-alternating.²⁵ The agreement is best for the choice of weights²⁶ $p_M=1, 3, 5, \dots$.

The choice of statistical weights may be further tested in two other ways. On the assumption that the general form of Eq. (2) has already been corroborated by the comparison plots of Fig. 7 it appears that the ratio of α_M to the corresponding Boltzman factor $e^{-W_M/kT}$ should yield a quantity proportional to \bar{p}_M . The multiplicative factor $|M|/M$ is used in the plot of this ratio against line number (Fig. 8) in order to obtain negative values of this ratio for the lines of the P branch.

The curve obtained is practically a straight line indicating that \bar{p}_M is a linear function of M as expected. The slight curvature is to be ascribed to the influence of the frequency term. A most important characteristic of the curve is that it practically passes through the origin so that \bar{p}_M must be proportional to M . This definitely excludes the series of values $p_M=2, 4, 6, \dots$.

For the vibration-rotation bands the summation rule leads to the same type of intensity variation for the choice of weights $p_M=1, 3, 5, \dots$, as

²⁵ Discussion under summation rule.

²⁶ The new quantum theory by admitting the state $m=0$ and integral rotational quantum numbers seems to require this choice also.

does Kemble's theory. For other choices however it may easily be verified¹⁵ that alternating intensities are prescribed.²⁷

Absolute intensities and transition probabilities. The absolute values of the absorption coefficients are given in Table II. Method I was used to yield absolute values of the coefficients for all lines in the positive branch, while

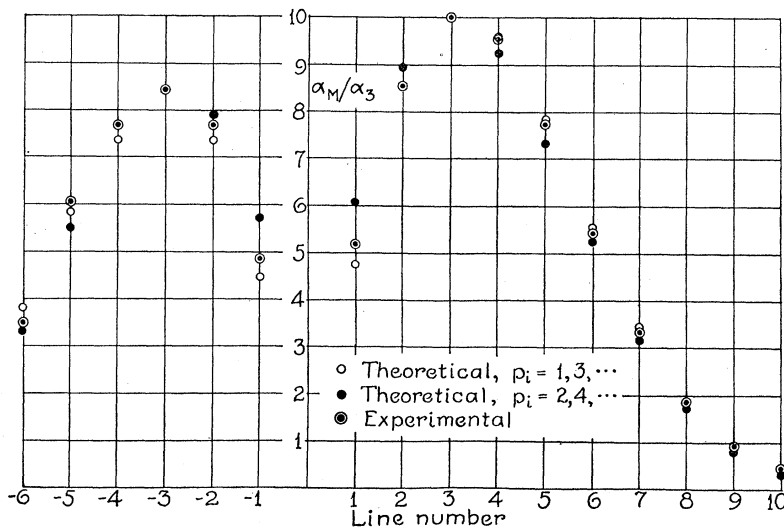


Fig. 7. Comparison of theory and experiment.

the other methods were used for the calculation of the single value for the line $M=3$. The best values of the absolute intensities,²⁸ namely those in the last column of the table were obtained by using the average value of α_3 as given by the methods listed in conjunction with the relative values derived from the ratio plots.

An important application of the data concerns itself with the Einstein probability-of-transition coefficients. It has often been shown that the integrated coefficient of absorption may be expressed in the form

$$a_M = h\nu_M N_i B_{i,f} / c \quad (18)$$

where the subscripts i and f refer to the initial and final states, $B_{i,f}$ is the Einstein coefficient of forced transition, ν_M is the frequency associated with

²⁷ If the HCl lines are unresolved doublets and not singlets as ordinarily supposed, it may be shown that the summation rule replaces \bar{p}_M by the sum $\bar{p}_M + \bar{p}_{M+1}$. The experimental data are therefore also in keeping with the assumption of a doublet line structure with the statistical weight series $\bar{p}_M = 2, 4, 6, \dots$, since the summation rule predicts the set of \bar{p}_M values $\bar{p}_M = 2, 2, 4, 4, \dots$ with this choice of \bar{p}_M . Mulliken's work on the correlation of the number of electrons in the molecule and the type of spectroscopic multiplet emitted (or absorbed) suggests a singlet structure in the HCl band spectrum.

²⁸ Tolman's estimates²⁸ are based on Imes' curves for a single tube length and are quite out of accord with the present results.

the transition $i \rightarrow f$ and N_i is the number of molecules in the state i . On evaluating N_i there is obtained after inverting formula (18)

$$B_{i,f} = \frac{\alpha_M c e^{W_i/kT} 8\pi I kT}{\nu_M \bar{p}_i N h} \quad (19)$$

The well known relation between the coefficients of forced and spontaneous transitions may be written

$$A_{f,i} = \frac{8\pi h \nu^3 \bar{p}_i B_{i,f}}{c^3 \bar{p}_f} \quad (20)$$

where $A_{f,i}$ is the coefficient of spontaneous transition and the other terms have the meanings attached previously. On combining Eq. (19) and Eq. (20) there results the following expression for calculating $A_{f,i}$ from the data.

$$A_{f,i} = \frac{(8\pi \nu_{i,f})^2 e^{W_i/kT} kIT \alpha_M}{c^2 \bar{p}_f N h^2}$$

Reference to Eq. (2) shows that neglecting frequency terms, $B_{i,f}$ and $A_{i,f}$ vary as \bar{p}_M/\bar{p}_i . The salient features of the dependence of the coefficients on line number are (a) the comparatively slight difference in value of the coefficients for various lines, (b) the identity of the limiting values of the two types of coefficients for the P and R branches. Conclusion (b) is subject to modification because of neglected frequency terms. $B_{i,f}$ is expected to vary with the inverse 4th power of the frequency and $A_{f,i}$ with the inverse first power.

The values²⁹ $B_{0,1} = 5.12 \times 10^{15}$ and $A_{0,1} = 58$, associated with the lines $M = 1$ and $M = -1$ respectively, were calculated from formulas (19) and (20.1). The value of $A_{0,1}$ (and the values of $A_{f,i}$ which may readily be calculated from it) are about ten times those of Tolman;²³ however even the values given here are rather smaller than might at first be expected. The low values appear to have given Professor Tolman³⁰ some concern at the time but are really bona fide and in harmony with the predictions of the correspondence principle, as will appear incidentally in the following discussion of the effective ionic charge.

Since the absolute intensities of the lines are determined by the variation in the electric moment which accompanies the vibration, the amplitude of the electric moment variation can be determined from the absolute absorption coefficients.

²⁹ The subscripts on the Einstein coefficients refer to the rotational quantum numbers for the states involved.

³⁰ The wide range of values of $A_{f,i}$; obtained by Tolman is due to his erroneous values for α_M . Several of his conclusions are therefore to be modified and certain of his laws may obviously be made more precise in view of the substantiation of eq. (2).

The electric moment denoted by $p(r)$ differs in value from the product of the nuclear separation and the charge on an electron because of the distortion of the Cl ion's symmetrical electronic configuration due to the presence of the H nucleus. The immediate object of this part of the paper will be to correlate the disturbing effect of the H ion with the distance apart of the nuclei. The calculation will first be carried through on the basis of the older form of quantum theory and as a first step the correspondence principle value for A_{01} is written³¹

$$A_{01} = \frac{16\pi^4\nu_{01}^3}{3hc^3} \bar{R}_{01}^2 \frac{\bar{p}_M}{p_M} \quad (21)$$

where \bar{R}_{01}^2 is a certain mean square value of the Fourier series component of the variable electric moment $p(r)$ associated with the transition giving rise to the line $M=-1$.

It may easily be shown that A_{01} is practically equal to the coefficient of spontaneous transition for a linear oscillator and that the effect of the rotational motion is very slight in modifying the value of R as calculated for the vibrational motion alone.

Practically all the usual methods of taking the average of R_{01}^2 for the linear oscillator as required in Eq. (21) lead to nearly the result

$$\bar{R}_{01}^2 = \frac{1}{2} R_{n=1}^2 \quad (22)$$

$$\text{or } = R_{n=1}^2 \quad (22.1)$$

where the assumption made for (22) is that the zero vibrational state is the initial state whereas the calculation for (22.1) supposes that the state $n = \frac{1}{2}$

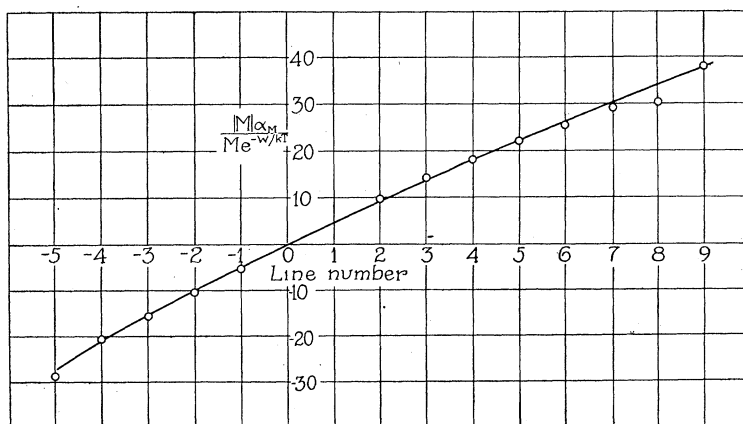


Fig. 8. Test of statistical weight choices.

is the lowest. The new formulation of the quantum theory leads to the relation $\bar{R}_{01}^2 = R_{n=1}^2$.

³¹ Cf. p. 811 for the presence of the factor $\bar{p}_M/p_M = 2$.

The analysis of the line spacing and position in the HCl bands yields the value³³ $r_0 = 1.28 \times 10^{-8}$ cm for the equilibrium separation of³² the nuclei and $\delta = 0.12r_0$ for the amplitude of vibration about the equilibrium position for one quantum of vibrational energy.

Neglecting the contribution of harmonic terms the value of $R_{n=1}$ is $(dp/dr)_{r=r_0}\delta$. The simultaneous solution of Eqs. (21) and (22) leads to an expression for $(dp(r)/dr)_{r=r_0}$ in terms of known constants. On defining the "effective charge" as $q = p(r)/r$ one may write $(dp/dr)_{r=r_0}$ as $q_0 + (dq/dr)_{r=r_0} r_0$.

Zahn's³³ data for the dielectric constant of HCl yields values of $p(r)$ when substituted into expressions correlating the value of the dielectric constant and electric moment. The assumption that all the dipoles are similar and oriented at random leads to the Debye³⁴ formula. Pauli³⁵ and Pauling³⁶ have treated the problem on the assumption of a space quantization assuming integral and half integral rotational quantum numbers respectively. The new quantum theory reproduces the values of the constants occurring in the classical Debye formula.

At ordinary temperatures nearly all the molecules are in the lowest vibrational state. The Debye equation, or the modifications mentioned, when applied to Zahn's data yield the value $\bar{p}(r) = q_0 r_0$ even if one half quantum of vibrational energy is assumed for the lowest state. It is therefore possible to estimate $(dq/dr)_{r=r_0}$ by combining Zahn's value of $q_0 r_0$ with $(dp(r)/dr)_{r=r_0}$ as calculated in this paper. Table IV contains the values of q_0 and $(dq/dr)_{r=r_0}$ calculated on the basis of the several theoretical variants mentioned.

TABLE IV

Calculation of q_0 and $(dq/dr)_{r=r_0}$

Entries under the headings *N* or *I* are calculated under the assumption of half integral vibrational quantum numbers for the first and integral values for the last.

	Classical and new quantum theory		Pauli theory		Pauling theory	
Apparent charge q_0 (Calculated from C. T. Zahn's data)	0.818×10^{-10}		$.300 \times 10^{-10}$		$.261 \times 10^{-10}$	
	<i>N</i>	<i>I</i>	<i>N</i>	<i>I</i>	<i>N</i>	<i>I</i>
$(dp(r)/dr)_{r=r_0} \times 10^{10}$	0.828	1.17	0.828	1.17	0.828	1.17
$(dq(r)/dr)_{r=r_0} \times 10^2$	0.008	0.196	0.414	0.679	0.442	0.71
$q_0/r_0 \times 10^2$	0.646	0.646	0.237	0.237	0.206	0.206

With the exception of the classical theory estimates and those depending on the new quantum theory it appears that the ratio $(dq/dr)_{r=r_0} : q_0/r_0$ is greater than 1 (Table IV). If the older form of the quantum theory be adhered to, the inference would be that somewhere near the origin the effective

³² E. C. Kemble, Jour. Opt. Soc. **12**, 1 (1926).

³³ C. T. Zahn, Phys. Rev. **4**, 400 (1924).

³⁴ P. Debye, Phys. Zeits. **13**, 97 (1912).

³⁵ W. Pauli, Zeits. f. Physik **6**, 139 (1921).

³⁶ L. Pauling, Proc. Nat. Acad. Sci. **12**, 32 (1926).

charge vs. nuclear separation curve is convex to the nuclear separation axis³⁷ or from another point of view that the formal continuation of the $q(r), r$ curve past the equilibrium point would intersect the $r=0$ axis below the $q(r)=0$ line. Consideration of simple models would suggest a positive value for the ordinate of the intersection point. The results seem, therefore, to be in harmony with the new rather than with the old quantum theory.³⁸

The writer wishes to thank Professor Lyman, Professor Pierce and Professor Chaffee for their kindness in placing the facilities of the Jefferson and Cruft Laboratories at his disposal and also to note his appreciation of the helpful advice of members of the Harvard faculty of Physics and Professor Bennett of Lehigh University. He is under special obligations to Professor Kemble who interested him in this subject and contributed many valuable suggestions.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY.
September 21, 1926.

Note added in proof, April 21, 1927.—In the interim since this paper was presented for publication the emphasis in modern physics has changed somewhat; so that references to the new quantum theory are to be interpreted in terms of 'wave' rather than 'matrix' bases. None of the conclusions of this paper are modified by this change in point of view.

³⁷ Since $q(r)=0$ for $r=0$.

³⁸ The results are in keeping also with the classical theory or with the assumption that the space orientation predicted by the older quantum theories is incomplete for small fields because of the disturbing influence of molecular collision though the last interpretation is not too plausible.