AUGUST 1, 1929 PHYSICAL REVIEW VOLUME 34

INTENSITIES IN THE HARMONIC BAND OF HYDROGEN CHLORIDE

BY J. L. DUNHAM
JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

(Received June 17, 1929)

ABSTRACT

Measurement of absorption intensities.—The intensities of the first nine lines of the negative branch of the first harmonic absorption band of HCl at 1.76μ have been measured with a prism spectrograph, using a galvanometer and thermo-relay to observe thermopile voltages. The positive branch, not being resolvable, was measured as a whole. The areas under the lines in a plot of percent absorption against frequency were obtained for 5 different tube lengths, namely 74.5, 25.0, 14.96, 9.90 and 4.88 cm and the integrated absorption coefficient of each line was calculated from the slope of the curve of area against tube length at the origin by methods developed by Bourgin. The probable error of the intensity measurements for the stronger lines was 6 percent.

Correlation with theory.—A calculation is made of the intensity ratio of the band as a whole to that of the fundamental based on a solution of Schrödinger's equation obtained by Morse for an anharmonic oscillator, and the value so obtained is within 6 percent of the experimental value. A second order perturbation calculation based on harmonic oscillator functions did not give concordant results. An unpublished analysis of the effect of rotation on the relative intensities of the lines in a band by Kemble is given and the relative intensities calculated for this band, giving agreement with experiment within 5 percent.

INTRODUCTION

THE discovery of the harmonic band of HCl at 1.76μ by Brinsmade and Kemble[1] was of importance in establishing the fact that the HCl molecule behaves as an anharmonic oscillator and in showing how this was to be interpreted on the basis of the quantum theory. Since then the constants of the molecule have been determined from the frequencies of the band lines[2, 3] and, in particular, the anharmonicity of the oscillator has been determined from the discrepancy between the spacing of the centers of the different bands as observed and the spacing predicted by the "one, two, three" rule for harmonic frequencies which one would expect classically. The harmonic bands would be entirely absent in the spectrum of an ideal linear oscillator, so that the intensities of the different harmonic bands provide another means of measuring the departure from harmonicity.

The work on intensities of absorption bands in this region is very meager because most measurements, using only one length of absorption tube, do not give an accurate estimate of intensities except under particular circumstances (see below in the discussion of Dennison's work), and in order to get good results it is necessary to adopt the more tedious procedure of using a

---

[1] J. B. Brinsmade and E. C. Kemble, Proc. Nat. Acad. 3, 420 (1917).

[2] E. S. Imes, Astrophys. J. 50, 251 (1919).

[3] "Report on Molecular Spectra in Gases," Nat. Res. Council., No. 57, 1927 especially pp. 52–68. This will be referred to hereafter as "Report."

number of different tube lengths and caluclating the absorption coefficients by a process involving extrapolation to zero length. Bourgin[4] has measured in this fashion the intensities of the lines of the absorption band at 3.46μ and this paper reports measurements on the first harmonic band at 1.76μ with essentially the same method and apparatus. The absorption of the first nine lines of the negative branch was measured for five different tube lengths, and their integrated absorption coefficient obtained by the methods developed by Bourgin[4], and in a similar fashion the intensity of the positive branch as a whole was measured. Owing to the fact that the positive branch was not sufficiently resolved to give reliable data for its component lines separately, the branch was treated as a whole. The theoretical intensities of the lines have also been calculated and agree satisfactorily with experiment.

EXPERIMENTAL WORK

The spectrometer and thermopile were the same which Bourgin[4] used and were set up in the same fashion, except that a larger prism was used which measured 9.8 cm wide by 6.7 cm high. The prism angle was 60°. The wave-length range falling on a slit 0.04 mm wide was about 17A and for slits this wide, the resolving power, which was just insufficient to resolve the isotopic doublets (separated by 14A), was limited principally by the size of the prism.

The source was an ordinary tubular 250-watt projection-bulb of the type sold commercially for portable moving-picture projectors. The filament is arranged in six parallel strands, all in a vertical plane so that when looked at edgewise, it appears to be a narrow and very intense strip of light. The energy from this source, in the region of 1.76μ was about twice that of a Nernst glower and it had the added advantage of being simple to operate. The current was supplied by a motor generator run by a synchronous motor from the 550-volt mains, so that there was no trouble from fluctuating intensity of the source.

The absorption tubes were of glass, about 5 cm in diameter and of five different lengths, namely 74.05; 25.0; 14.96; 9.90; and 4.88 cm. The windows on the ends were of fused quartz, optically flat and about 1.5 mm thick. The light beam from the source passed through a focus in the tube so that the beam never acquired a diameter of more than 2 cm inside the tube, and, as the tubes were 5 cm in diameter, it was not necessary to insert diaphragms or to make other provisions to reduce reflections from the side walls.

The HCl was generated by dropping concentrated sulphuric acid on pure NaCl, and passing the gas through concentrated sulphuric acid to dry it before passing it into the absorption tube. Between the generator and the tube there was only one short length of rubber tubing, all the rest being glass and, as the gas was passed through rapidly, the chance of contamination by the rubber was slight. The exact correspondence of the curves obtained with those of other workers in this region [1, 2] was taken as evidence that the HCl was pure.

The thermopile was the same Coblentz, silver-bismuth, twenty-six junction thermopile which Bourgin used. It was enclosed in a glass tube which

---

[4] D. C. Bourgin, Phys. Rev. **29**, 794 (1927).

was evacuated by an ordinary "Cenco" pump. The current from the thermopile was observed by a thermo-relay manufactured by Kipp & Sons in Holland. The primary galvanometer, connected directly to the thermopile, was a Kipp instrument with a sensitivity of 1.2×10^{-9} amps. per mm and the secondary galvanometer (or observing galvanometer) was a Weston, gravity controlled, moving coil instrument with a sensitivity adjustable between 10^{-9} and 10^{-11} amps. per mm and ordinarily used in these experiments at a sensitivity a little below 10^{-10} amps. per mm. With these galvanometers the limit to the total sensitivity attainable with the relay was set by the Brownian movement[5] of the primary galvanometer which became noticeable at sensitivities of about 10^{-12} amps. per mm. The set was used just short of that point. It was found necessary to shield the entire primary galvanometer circuit against magnetic disturbances, as random magnetic fluctuations induced appreciable currents in the circuit. Zero-drift troubles were obviated by having the spectrometer and galvanometers in a separate room from the observer and source, and by thoroughly lagging the thermopile.

The absorption tubes were mounted on a rack which could be swung back and forth so that the tube was either in or out of the light path. A dummy tube, not filled with HCl though otherwise just like the others, was also mounted on the rack, so that when the filled tube was not in the light path the dummy was. For a given spectrometer setting the absorption was measured by rapidly interchanging the filled and dummy tubes and noting the resulting deflection of the galvanometer. This gives ΔI the amount of energy absorbed. The total intensity, I, of the beam could then be measured by closing a shutter in front of the entrance slit of the spectrometer while the dummy tube was in the beam, and the ratio $\Delta I/I$ gives the percent absorption. Inasmuch as there are no absorption bands of air, water vapor, or CO_2 in the region around 1.76μ of sufficient intensity to be observable, it was not considered necessary to evacuate the dummy tube. It was also assumed that there was no appreciable selective reflection from the tube windows.

The positions of the spectrometer were read from a dial on the end of a rod which was attached to the tangent screw of the spectrometer so that the table could be turned from the observers position in front of the galvanometer telescope. The readings of this dial could be calibrated in terms of frequency by two methods. One method was to calibrate the dial by the divided scale on the table and then go over to frequency by the usual formula for the dispersion of a prism, and the known refractive index of quartz in this region, and the other method was to compare the separation of the peaks of the lines in the negative branch in dial degrees with their frequency separation as given by Imes.[2] The mean of the results of these two methods was used.

CALCULATIONS

The absorption of light in a gas follows the exponential law so that if I_0 is the initial intensity of the beam and I the intensity after having passed through a certain length x of gas, then $I/I_0=e^{-\mu x}$, where μ is the coefficient of absorption. μ, of course, is a function of frequency. The intensity of a

---

[5] Ising, Phil. Mag. 1, 827 (1926).

line,[6,7] or the integrated absorption coefficient α, is defined by the equation $\alpha=\int_0^\infty \mu(\nu)d\nu$, the integral being taken over the line in question. The percent absorption for any given frequency is given by $(1-I/I_0)=1-e^{-\mu x}$ and the area, $A(x)$, under a line is given by $\int_0^\infty (1-e^{-\mu x})d\nu$, from which one can immediately verify that

$$\alpha=\left(\frac{dA}{dx}\right)_{x=0}=\int_0^\infty \mu(\nu)d\nu.$$

This explains the necessity of using a number of different tube lengths and calculating the areas under the lines in order to get the true intensity. Dennison[8] has developed a theory for calculating the relative absorption coefficients of the lines in a band from observations on one tube length, but he assumes that the tube length is great enough that the absorption at the center of the line is nearly complete. To have fulfilled this condition for the harmonic band would have required impracticably long absorption tubes, since the greatest absorption for the 75 cm tube was only 31 percent. In his work there are also a number of special assumptions about line shape and slit width so that it is open to question whether his theory would give reliable results even if the absorption were sufficiently intense. Besides, Dennison's method, giving only relative coefficients for the lines in a band does not make it possible to use only one tube length if absolute intensities are desired.

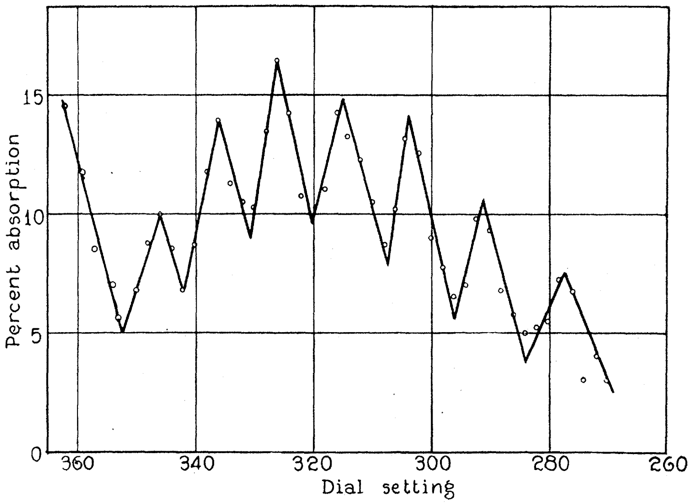

Fig. 1. Percent absorption plotted against spectrometer dial setting.

The percent absorption was plotted against dial settings, of which a typical curve is shown in Fig. 1. In view of the closeness of the peaks it was decided to draw the best straight lines through the points on each side of a peak. The area could then be calculated by considering each line as a trapezoid superposed by a triangle. Of course the area under a line strictly

---

[6] R. C. Tolman, Phys. Rev. **23,** 693 (1924).

[7] E. C. Kemble, Phys. Rev. **25,** 1 (1925).

[8] Dennison, Phys. Rev. **31,** 511 (1928).

speaking extends over an infinite frequency range. However, it is a good approximation to assume that the line area is given by the area bounded by successive minima because, where the heights of successive peaks change linearly with frequency the net loss in area by overlapping is zero, and where the peak heights are not linear in frequency, the change in height is small enough that there would be no appreciable correction.

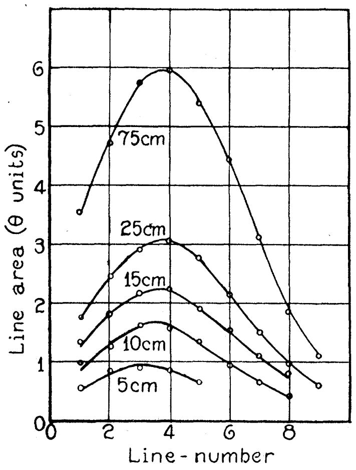

Fig. 2. Areas under absorption curves plotted as function of ordinal numbers of lines.

The areas determined were plotted as a function of ordinal number (Fig. 2), one plot to each tube length, and the best smooth curve drawn through the points. The areas of the various lines were then read from the smoothed curves, so that the area of a line was checked against that of its neighbors. In Table I are given the areas both "smoothed" and "unsmoothed." These "smoothed" areas were plotted against tube length, one plot for each line of which Fig. 3 is a sample, and it was the slope of these lines at the origin that gave α.

TABLE I. *Areas under absorption curves for tubes of various lengths. "O" heads columns of the original, "unsmoothed" areas; "S" heads columns of areas as read from "smoothing curves" of the type shown in Fig. 2.*

	75 cm		25 cm		15 cm		10 cm		5 cm	
Line No.	*O*	*S*	*O*	*S*	*O*	*S*	*O*	*S*	*O*	*S*
1	355	345	176	176	135	127	100	85	56	50
2	471	477	246	246	182	185	128	131	87	80
3	575	572	292	295	216	216	164	163	90	94
4	597	597	309	309	224	221	156	163	86	87
5	540	547	279	279	191	191	135	131	68	63
6	444	444	216	216	155	152	98	99		
7	318	318	150	150	113	109	67	68		
8	185	190	98	98	83	75	44	43		
9	113	113	63	63						

Bourgin has developed two analytical methods for getting the slope of these curves at the origin, and they are superior to graphical or Taylor-series methods because they make greater use of the part of the curve lying at a distance from the origin in determining its slope at that point. That is to say, they use *all* the data to derive α instead of depending largely on the two shortest tube lengths.

The first method[3] gives only the ratio of the α's of a given line to that of a standard line, and does not give the absolute value of α. The basic assumption is that all the lines have approximately the same shape, though it is not necessary to specify what shape, and then it can be shown that if x'_m and $x'_{m'}$ are values of the abscissae for the given line (m) and the standard line (m') which have the *same ordinate*, then

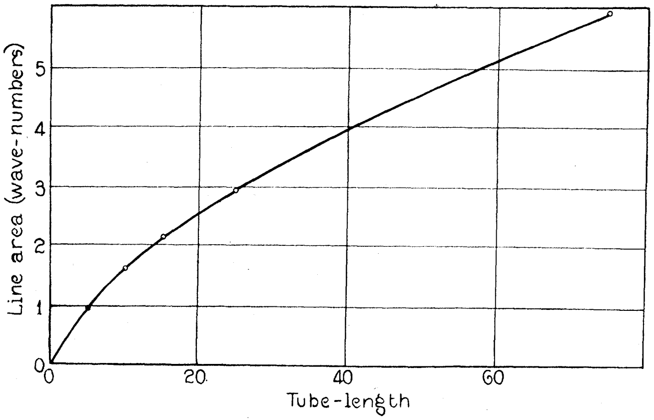

Fig. 3. "Smoothed" area as a function of tube length.

$$\lim_{x_m \to 0} \frac{x'_{m'}}{x'_m} = \frac{\alpha_m}{\alpha_{m'}} .$$

Fig. 4 is a graph of $x'_{m'}/x'_m$ for the various lines referred to line 3 as a standard, and the extrapolation of the curves to the axis of ordinates is the ratio of α_m to α_3. Bourgin discusses at some length the theoretical curvature of these curves on the assumption that the absorption lines are really close, unresolved, doublets, due to the existence of the two isotopes of chlorine,[9]

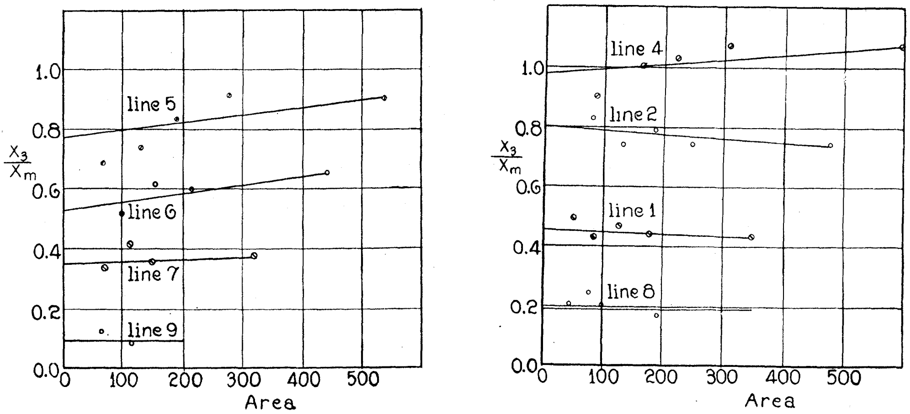

Fig. 4. Graph of $x'_{m'}/x'_m$ for various lines, referred to line 3 as a standard.

---

[9] F. W. Loomis, Astrophys. J. 52, 248 (1920).

but for numerical values it is a good approximation to use straight lines. The relative values of the coefficients obtained in this manner are tabulated in Table II.

TABLE II. *Relative values of integrated absorption coefficient. α is in frequency units per centimeter tube length; b is in frequency units. Columns 2 and 3 are respectively, absolute and relative values as given by method II; Column 4 gives relative values as given by method I; Column 5 is weighted average of Columns 3 and 4.*

Line No.	$\alpha \times 10^{-10}$	α_m/α_3	α_m/α_3	α_m/α_3	calc. ratio	A_m^2/A_3^2	$b \times 10^{-10}$
		method II	method I	ave.			
1	0.329	0.494	0.468	0.485	0.501	0.360	1.37
2	0.574	0.862	0.796	0.840	0.859	0.696	1.42
3	0.666						1.146
4	0.620	0.931	0.961	0.941	0.942	1.087	1.92
5	0.500	0.751	0.737	0.746	0.755	0.914	1.99
6	0.348	0.522	0.521	0.522	0.503	0.603	
7	0.205	0.324	0.338	0.329	0.325	0.308	
8	0.118		0.177	0.177	0.181		
9	0.057		0.085	0.085	0.088		
R branch	4.14	6.21			5.91		

Bourgin's second method[10] assumes a definite shape for the lines, namely that $\mu = a/[(\nu - \nu_2)^2 + b^2]$ where a and b are disposable constants and ν_1 is the frequency of the center of the line. Let $\psi(y) = \int_0^\infty (1 - e^{-ay/(\nu 2 + b 2)}) d\nu$; then ψ is fitted to the experimental A by changing the scale of y and in this way a condition is obtained for a and b. From these, α is directly calculated by the simple expression $\alpha = \pi a/b$. The half-width of the line is b. The values of α and b obtained by this method are tabulated in Table II.

The positive branch was not resolved sufficiently to get individual line-areas from it, so the branch was measured as a whole and its absorption coefficient obtained graphically from a curve of the type shown in Fig. 4. This value is also given in Table II.

Dennison's work can be used, as already mentioned, to calculate the relative absorption coefficients of the lines in a band. He arrives at a formula (reference 8, p. 510) for the area under an absorption line, which is essentially $A^2 = K\alpha x$ where K is a constant, and this shows at once that the approximations he used are not good at short tube lengths, since according to the formula, $(dA/dx)_{x=0}$ is infinite. For a given length of tube this formula indicates that α is proportional to A^2, so $A^2{}_m/A_3^2$ was calculated from the data on the 75 cm tube and the values are given in Table II. These, of course, should be the ratio of the intensities of the different lines in comparison to that of line 3, but the divergence from the relative intensities calculated by Bourgin's methods and from the theoretical intensity ratios is sometimes more than twenty percent, which means that Dennison's approximations are not good for bands of such small intensity as this one.

ACCURACY

There were two principal sources of error in the measurements. The first was the limit of precision to which the galvanometer could be read. The mean deviation from the mean of 75 galvanometer readings was 0.3 mm and

---

[10] D. C. Bourgin, Phys. Rev. **32**, 237 (1928). Bourgin assumes several specific shapes, but arrives at the conclusion that this one is the best.

this is 7 percent of the average galvanometer deflection (4 mm). Of course, for the stronger lines and the longer tubes, the percent error was somewhat less, and for the weak lines and the short tubes somewhat more. The fact that four readings were taken at each point makes the corresponding probable error in the determination of one point 3.5 percent.

The second main source of inaccuracy was a zero error. It was found that the deflection on exchanging tubes with the spectrometer set for a wavelength outside the band, was not zero and this residual deflection changed from time to time. It was impossible, on this account, to avoid an error of about 5 percent in the absorption values.

A consideration of the effect of these errors on the areas, the fact that each band was measured four times, and the effect of smoothing in increasing the accuracy, indicates that these two major sources of inaccuracy would give a probable error of 5 or 6 percent to the value of α for line 3. It is not to be expected that the less intense lines would have as high a degree of accuracy, but in view of the smoothing to which the data were subjected the error is not to be considered as being proportional to the faintness of a line.

CORRELATION WITH THEORY

The first matter of interest in a discussion of the relation between the experimental data and the theoretical intensities is that of the intensity of the band as a whole. To find the theoretical intensity it is necessary to calculate the matrix component of the electric moment for the two vibrational states involved, namely the states 0 and 2, and to do this we must know the wave functions for these two states. Morse[11] has obtained an exact solution of Schrödinger's equation for an oscillator with a potential function composed of exponentials. The wave functions he obtains are to be preferred to those obtained by perturbation methods because with them the computation of intensities is less tedious. Morse has shown that his analysis gives the correct energy level formula, namely

$$E_n = h\nu_0(n+\tfrac{1}{2}) - h\nu_0 x(n+\tfrac{1}{2})^2 \qquad (1)$$

where n is the vibrational quantum number; ν_0 is the frequency of a small classical vibration about the equilibrium point and x is the usual constant of anharmonicity, so these functions may be supposed to give correct intensity relations also.

The potential function which Morse introduces is

$$U(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) \qquad (2)$$

where D is the energy of dissociation, r the nuclear separation, r_0 the equilibrium value of r and a a disposable constant. This function has a minimum at $r=r_0$, approaches zero asymptotically as r becomes infinite and has a very large value (not infinite) when $r=0$. It is therefore of the correct general shape, and by a proper choice of D, a, and r_0 can be made to fit the data of any particular molecule quite well.

---

[11] P. M. Morse. To appear shortly. Dr. Morse kindly supplied Professor Kemble with a manuscript copy, which I have used.

Schrödinger's equation for the radial part of the wave function of a rotating oscillator may be thrown into the form

$$\frac{d^2R}{dr^2}-\frac{j(j+1)R}{r^2}+\frac{8\pi^2\mu}{h^2}(E-U)R=0 \tag{3}$$

where, if X is the radial part of Ψ, $R=rX$ and $\mu=m_1m_2/(m_1+m_2)$, is the ordinary mass coefficient. Morse has worked out the solution, R_n, if (2) is used for the potential function, and the term $j(j+1)R/r^2$ is omitted as being small (cf. below in the discussion of relative intensities). His solution is

$$R_n(r)=A_ne^{-(k/2)e^{-a(r-r_0)}}\left[ke^{-a(r-r_0)}\right]^{(k-2n-1)/2}L_{kn}(ke^{-a(r-r_0)}) \tag{4}$$

where $k=4\pi(2\mu D)^{1/2}/ah$ and $L_{kn}(ke^{-a(r-r_0)})$ is a polynomial in $(ke^{-a(r-r_0)})$, closely related to the generalized Laguerre polynomial and defined by

$$L_{kn}(x)=x^n-n(k-n-1)x^{n-1}+\tfrac{1}{2}n(n-1)(k-n-1)(k-n-2)x^{n-2}\cdots$$

A_n is given by the formula

$$A_n=\left(\frac{a(k-2n-1)}{n!(k-n-1)\Gamma(k-n-1)}\right)^{1/2}.$$

The constants a and k appearing in (4) are related to the observable spectroscopic constants by the relations

$$a=(8\pi^2\mu c\nu_0x/h)^{1/2} \qquad k=1/x \tag{5}$$

where ν_0 is in wave-numbers and x is the anharmonicity constant appearing in the energy-level Eq. (1).

With these wave functions we are in a position to calculate the matrix component of the electric moment of the molecule for the transition 0→2. The electric moment $p(r)$ is a function of the nuclear separation and, for HCl, may be assumed to be linear in r within the range of r for which the wave functions are noticeably different from zero. So we can express $p(r)$ as $p(r_0)+(r-r_0)(dp/dr)_{r=r_0}$ or, if we let $(dp/dr)_{r=r_0}=p_0'$, $p(r)=p(r_0)+(r-r_0)p_0'$. The matrix component P_{nm} of p is given by $\int pR_nR_mdr$, and, if we change to the variable $u=r-r_0$, we have, due to the orthogonality of the R's

$$P_{nm}=p_0'\int_0^\infty uR_nR_mdu. \tag{6}$$

Substituting the values of R given in (4), one has

$$P_{02}=p_0'A_0A_2k^{k-3}\{k^2J_{k-1}-2k(k-3)J_{k-2}+(k-3)(k-4)J_{k-3}\} \tag{7}$$

where $J_{k-i}=\int_{-\infty}^{\infty}e^{-ke^{-au}}e^{-(k-i)au}udu$.

To evaluate these integrals one first makes the transformation $x=e^{-au}$ under which J becomes

$$J_{k-i}=-(1/a^2)\int_0^\infty e^{-kx}x^{k-i-1}\log xdx. \tag{8}$$

Inspection shows that (8) can be expressed as

$$J_{k-i}=\frac{1}{a^2}\,\frac{d}{di}\left(\int_0^{\infty}e^{-kx}x^{k-i-1}dx\right)=\frac{1}{a^2}\,\frac{d}{di}\left(\frac{\Gamma(k-i)}{k^{k-i}}\right) \tag{9}$$

$$=\frac{1}{a^2}\,\frac{\Gamma(k-i)}{k^{k-i}}(\log k-\psi(k-i))$$

where $\psi(x)=d\log\Gamma(x)/dx=\Gamma'(x)/\Gamma(x)$. $\psi(x)$ can be expressed as a sum[12,13]

$$\psi(x)=-C+\sum_{s=0}^{\infty}\left(\frac{1}{s+1}-\frac{1}{x+s}\right) \tag{10}$$

where C is Euler's constant, but this summation is not in a form suited to numerical computation. A much more manageable form of (10) can be employed if x is an integer, say n, in which case (10) can be written

$$\psi(n)=-C+\sum_{i=1}^{n-1}\frac{1}{i}\cdot \tag{10a}$$

This summation can be evaluated approximately to a high degree of accuracy by the formula

$$\sum_{i=1}^{n-1}1/i\cong C+\log\left((n-1)+\tfrac{1}{2}\right). \tag{11}$$

We are using n in the neighborhood of 50 and for such values this approximation is good to one part in a hundred thousand. Now the right hand side of (11) is defined for non-integral values of n, and, in view of the regularity of (10), one can use (11) as an interpolation formula for finding $\psi(x)$ when x is not an integer, giving

$$\psi(x)\cong\log\left(x-1+\tfrac{1}{2}\right) \tag{10b}$$

We now return to the J's and substitute (10b) in (9) which gives

$$J_{k-i}=\frac{1}{a^2}\,\frac{\Gamma(k-i)}{k^{k-i}}\log\left(\frac{k}{k-i-\frac{1}{2}}\right). \tag{12}$$

Substituting (12) in (7) the latter becomes

$$P_{02}=p_0'A_0A_2k^{k-3}\left\{\log\left(\frac{k}{k-1\frac{1}{2}}\right)-2\frac{k-3}{k-2}\log\left(\frac{k}{k-2\frac{1}{2}}\right)+\left(\frac{k-4}{k-2}\right)\log\left(\frac{k}{k-3\frac{1}{2}}\right)\right\} \tag{13}$$

and it is only necessary to substitute the numerical values of a and k in (13) to get P_{02}. The spectroscopically determined constants of HCl are [14,15]

$\nu_0=2940.7\ \text{cm}^{-1}$ $\quad r_0=1.279\times10^{-8}$ cm

$\nu_0x=\ 53.58\ \text{cm}^{-1}$ $\quad J_0=2.645\times10^{-40}\ \text{cm}^2$ gm

and these values when substituted in (5) give

$$a=1.777\times10^{-8}\ \text{cm}^{-1}\qquad k=54.885. \tag{14}$$

---

[12] Nielsen, Handbuch der Gammafunktion: B. G. Teubner, p. 15.

[13] Jahnke und Emde, Funktionentafeln: B. G. Teubner, p. 27.

[14] Birge, Report, p. 230.

[15] E. C. Kemble, Jour, Opt. Soc. Am. **12**, 1 (1926).

P_{02} can now be calculated and is

$$P_{02}=7.16\times10^{-11}\ p_0' \tag{15}$$

Similarly the matrix component P_{01} for the fundamental band can be calculated giving

$$P_{01}=7.67\times10^{-10}\ p_0' \tag{16}$$

Now α the absorption coefficient, is connected to the P's by the equation

$$\alpha_{nm}=\text{const.}\times\bar{p}\times e^{-E''/kT}\nu_{nm}(P_{nm})^2 \tag{17}$$

where $\bar{p}$ is the average of the statistical weights of the initial and final states; E'' is the energy of the initial state, and ν_{nm} is the frequency associated with the transition. If we compare corresponding lines in two bands, the ratio of their α's is given by

$$\left(\frac{\alpha_{02}}{\alpha_{01}}\right)_{calc.}=\frac{\nu_{02}}{\nu_{01}}\left(\frac{P_{02}}{P_{01}}\right)^2=1.983\times\left(\frac{.716}{7.67}\right)^2=0.0173. \tag{18}$$

The experimental value of this ratio is readily calculated. From Bourgin's[4] data the intensity of the third line in the negative branch of the fundamental band is 41.3×10^{-10} and from Table II the intensity of the same line in the harmonic band is 0.666×10^{-10}. So

$$\left(\frac{\alpha_{02}}{\alpha_{01}}\right)_{exp}=\frac{0.666}{41.3}=0.0161. \tag{19}$$

These two results differ by only 6 percent which is within the limits of experimental error.

The original justification for supposing that Morse's potential function (2) would fit the facts adequately for HCl was that the energy level formula given by Morse is of the right form. As far as vibrational energy levels are concerned, it is accurate, but when the information given by the rotational energy levels as to the shape of the potential function is taken into account, certain discrepancies are found. If we let $(r-r_0)/r_0=\xi$, then we can express U in the form

$$U(\xi)=K\xi^2(1+a\xi+b\xi^2+c\xi^3+\cdots),$$

and it is possible to compute K, a, b, and c from the rotational and vibrational energy levels. Kemble [15] has computed these constants for HCl on the basis of the Bohr theory, and Fues,[16] applying second order perturbation theory to an harmonic oscillator, has shown that at least K, a and b are the same as those given by the Bohr theory. Consequently Kemble's evaluation of these constants can be taken over into the wave mechanics.

To compare Morse's potential function with that given above, it is only necessary to expand (2) in powers of ξ about $\xi=0$ and compare coefficients. The numerical values of the coefficients obtained in these two fashions are:

[16] E. Fues, Ann. d. Physik **80,** 396 (1926).

	Morse	Kemble
a	-2.27	-2.421
b	3.00	3.905
c	-2.93	-2.86

The constants a and b as obtained from the two analyses are seen to be materially different, and it is an interesting question, therefore, how accurate the intensity calculation based on Morse's wave functions would be. It is not possible to distinguish between the intensities given by Morse's method and the values determined experimentally, because the former do not fall outside the limits of accuracy of the measurements, so an attempt was made to see if a calculation of the intensities considering the molecule as a perturbed harmonic oscillator would give different results. The third and fourth power terms in ξ were introduced as perturbing terms and a second order perturbation carried out on the wave functions. The intensity calculated in this fashion was 60 percent higher than the experimental value, and it appeared that it would be necessary to carry out a third order perturbation to obtain precise results as the process does not converge rapidly.

The relative intensities of the lines in a band are more easily calculated, to a first approximation, as the contribution to each from the vibration is the same and hence cancels in considering only relative values. The two most important factors which vary from line to line are the Boltzmann factor and the statistical weight. Kemble[6] has shown that the average of the statistical weights for the initial and final states should be used and arrives at the formula $\alpha = \text{Const} \times \bar{p} e^{-E''/kT} f(\nu)$ where $f(\nu)$ is a small correction term depending on the frequency and is due, largely, to the effect of centrifugal force on the oscillator. This function has been worked out by Kemble for the harmonic band, but, as his work has not been published, I shall give the analysis here.

We go back to Eq. (3), retaining, this time, the term in j, j being the rotational quantum number and R the vibrational wave function obtained from the entire wave function Ψ, by the relation $\Psi(r\theta\phi) = (R(r)/r)\, Y(\theta\phi)$. The individual wave functions have two subscripts, one referring to the particular characteristic value which E (in Eq. (3)) takes on and the other to j. We shall assume that Eq. (3) with the term in j left out has been solved and wave functions R_{n0} obtained, though it will not be necessary to give these functions explicitly. The effect of the term in j upon these functions can then be determined by considering it as a perturbation.

According to the ordinary procedure in perturbation problems[17] we start from the fact that Eq. (3) is of the type

$$L(R) - \lambda M_j(r) R + \beta E R = 0 \qquad (20)$$

where $L(R)$ is a self-adjoint differential expression; $\lambda M_j = j(j+1)/\beta r^2$ and $\beta = 8\pi^2\mu/h^2$. The wave functions and energy levels are expanded in a series in λ

---

[17] A. Sommerfeld, Wellenmechanischer Ergänzungsband p. 170 ff.

$$R_{kj}=R_{k0}+\lambda u_{kj} \qquad (21)$$
$$E_{kj}=E_{k0}+\lambda\epsilon_{kj}$$

u_{kj} can be given by

$$u_{kj}=\sum_{i=0}^{\infty} {}_j\gamma_{ki}R_{i0},$$

where

$$_j\gamma_{ki}=\frac{_jC_{ki}}{E_k-E_i}=\frac{1}{E_k-E_i}\int M_j R_{i0}R_{k0}\,dr,$$

so that

$$R_{nj}=R_{n0}+\sum_i{}'\frac{R_{i0}}{E_n-E_i}\int\frac{j(j+1)}{\alpha r^2}R_{n0}R_{i0}\,dr, \qquad (22)$$

where $\sum_i{}'$ means that in summation the term for which $i=n$ shall be left out. We are, of course, interested in the matrix component of the electric moment $p(r)$ given by

$$P_{n'j'n''j''}=\int p(r)R_{n'j'}R_{n''j''}dr \qquad (23)$$

Introducing the abbreviation

$$S_{ni}=\frac{1}{\beta}\int\frac{R_{n0}R_{i0}}{r^2}dr,$$

and substituting (22), (23) can be written

$$P_{n'j'n''j''}=\int p(r)R_{n'0}R_{n''0}\,dr$$
$$+\int p(r)\left\{R_{n'0}j''(j''+1)\sum_l{}'\frac{S_{n''l}R_{l0}}{E_{n''}-E_l}+R_{n''0}j'(j'+1)\sum_l{}'\frac{S_{n'l}R_{l0}}{E_{n'}-E_l}\right\} \qquad (24)$$

The last step assumes that in Eq. (22) the terms in S are small compared with those in R_{n0} and that consequently in (24) the products of two terms in S will be negligible, this assumption being justified by the fact that the rotational distortion of intensities is small.

If we define I by

$$I_{n'n''}=\int p(r)R_{n'0}R_{n''0}\,dr, \qquad (25)$$

it is easily verified that, owing to the orthogonality of the R_{n0}'s, and the fact that they are normalized, $I_{nn}=p_0$ and $I_{nm}=p_0'\int rR_{n0}R_{m0}\,dr$. That is to say, the I's are simply the matrix components of the transitions for the unperturbed anharmonic oscillator. Again, since $(r-r_0)/r_0$ is small compared to 1 whenever Ψ is appreciable, $1/r^2$ can be expanded in a series about r_0 and the expressions for S simplified, the result being

$$S_{nm}=-\frac{2}{\beta r_0{}^3}\frac{I_{nm}}{p_0'} \quad \text{if} \quad n=m$$
$$=-\frac{1}{\beta r_0{}^2} \qquad\quad \text{if} \quad n=m \qquad (26)$$

Substituting these expressions for S and I in (24) gives

$$P_{n'j'n''j''}=I_{n'n''}-\frac{2}{\beta r_0^3 p_0'}\sum_l{}''' I_{n'l}I_{n''l}\left\{\frac{j'(j'+1)}{E_{n'}-E_l}+\frac{j''(j''+1)}{E_{n''}-E_l}\right\}. \tag{27}$$

In substituting the values for the harmonic band where $n'=2$ and $n''=0$, we know experimentally that $I_{03}\ll I_{00}$ and it is evident that $I_{00}\cong I_{11}\cong I_{22}$, so we need consider only 3 terms in (27) (i.e. $l=0$, 1 and 2) and, if we substitute $E_n-E_m=h\nu_0(n-m)$ and carry out the summation over three terms, we get

$$P_{2j'0j''}=I_{20}-\frac{2}{\beta r_0^2 p_0'}\left[\frac{I_{20}I_{00}}{2h\nu_0}j'(j'+1)\right.$$
$$\left.+\frac{I_{21}I_{01}}{h\nu_0}\{j'(j'+1)-j''(j''+1)\}-\frac{I_{22}I_{02}}{2h\nu_0}j''(j''+1)\right] \tag{28}$$

Now $1/h\beta r_0^2=B_0$ and $B_0(j'(j'+1)-j''(j''+1))=\nu-\nu_c$ where ν_c is the frequency of the center of the band, and if we substitute this relation, together with the value of I_{00}, into Eq. (28) we have

$$P_{2j'0j''}=I_{20}\left[1-\frac{2(\nu-\nu_c)}{r_0p_0'v_0}\left\{\frac{p_0}{2}+\frac{I_{21}I_{01}}{I_{02}}\right\}\right]. \tag{29}$$

The second term in the square bracket is small compared to the first so that, in taking ratios of the P's we can expand in series and omit second order terms. If we let

$$a=\frac{2}{r_0p_0'\nu_0}\left\{\frac{p_0}{2}+\frac{I_{01}^2}{I_{02}}\right\},$$

then $P_{2j'0j''}=I_{02}[1-a\Delta\nu]$. By Eq. (17) we have the relation

$$\begin{aligned}\frac{\alpha_{02m}}{\alpha_{023}}&=\frac{\nu_m}{\nu_3}\,\frac{I_{02}^2}{I_{02}^2}\,\frac{[1-a\Delta\nu_m]}{[1-a\Delta\nu_3]}\,\frac{\bar{p}_m}{\bar{p}_3}e^{-(E_m''-E_3'')/kT}\\&=\frac{\nu_m}{\nu_3}\{1+2a(\Delta\nu_3-\Delta\nu_m)\}\frac{\bar{p}_m}{\bar{p}_3}e^{-(E_m''-E_3'')/kT}\end{aligned} \tag{30}$$

Taking the values of ν and ν_c from Imes' work,[2] that of p_0 from Bourgin's paper and using the empirical values of I_{01} and I_{02} as found, respectively, in Bourgin's paper and in this one, α_m/α_3 was calculated for the first nine lines of the negative branch and the values so obtained are tabulated in Table II column 6 and a graph of the values of the ratio of the calculated to observed values of the α's is given in Fig. 5. The difference between observed and calculated values is never over 4 percent and the extreme range of the points is only 5 percent. The mean of the ratio's of the calculated to experimental values is within 1.5 percent of being 1.

In Table II the values of b, the half-width of the lines, are given for the first five lines as calculated from Bourgin's second method. Owing to the steepness of the curves, this method does not give b with any precision, as can easily be seen from the great spread of the values. The increase of the isotope doublet separation[9] is the obvious place to look for a cause of the increase in b with ordinal number. On the basis of Loomis' formula for isotope separation[18] one can readily calculate that in the first five lines of the negative branch of this band the change in separation of the doublet would be three or four percent of the total separation. The tabulated values of b are the widths of a symmetrical, somewhat arbitrarily shaped line which is made to fit the actual doublet. If the small satellite line materially overlaps the larger one, it is possible that the value of b would be extremely sensitive to the doublet separation. Without going into a quantitative treatment of this broadening which would, at best, be extremely cumbersome, one can say that the observed increase of b with line number seems plausible.

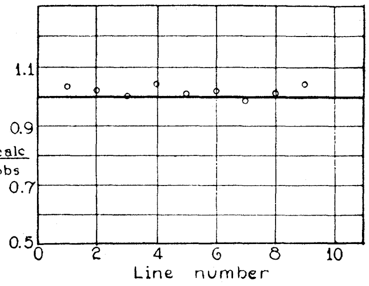

Fig. 5. Graph of the values of the calculated and observed values of the α's.

The author wishes to acknowledge his indebtedness to Professor E. C. Kemble who interested him in the subject and whose advice and suggestions have been indispensable in carrying out this research.

---

[18] F. W. Loomis, Report, p. 260 ff.