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INTENSITIES OF VIBRATION-ROTATION BANDS WITH SPECIAL REFERENCE TO THOSE OF HCL

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ABSTRACT

Intensity formula for vibration bands. The intensities of vibration bands depend on certain matrix elements of the electric moment of the molecule. The electric moment of a diatomic molecule is a function of the nuclear separation and must be expanded in a power series about the equilibrium point. Matrix elements are calculated by perturbation methods for the fundamental and first two harmonic bands of the vibration spectrum, and it is found that, to a first approximation, for the n^{th} harmonic it is necessary to consider the $(n+1)^{th}$ power in the series expansion of the electric moment, and higher powers for better approximations. The formulas for the fundamental and first harmonic are given to a second approximation. The matrix elements are also calculated from wave functions due to Morse for a diatomic molecule, and it is shown that there is a negligible difference between the two methods of calculation for small quantum numbers. Formulas are also given for the ratio of the intensity of the first two harmonic bands to that of the fundamental.

Application to HCl. The formulas derived in the first part are applied to the case of HCl which is the only molecule for which the intensities of the vibration bands have been measured with any precision. New data from wave-length measurements of Meyer and Levin are used and the value of the coefficient of the quadratic term in the power series expansion of the electric moment is found. It is found that two values of this coefficient would give the same intensities and no satisfactory way of resolving the ambiguity is available. Numerically it is found that if the electric moment $p=p_e+p_e'\xi+p_e''\xi^2/2$, then $p_e''=0.070\times10^{-18}$ or 4.56×10^{-18} e.s.u.

INTRODUCTION

I HAVE recently shown[2] that the ratio of the measured intensities of the fundamental and harmonic bands of HCl in the near infrared can be predicted quantitatively assuming Morse's[3] vibrational wave function analysis and also that the electric moment of the molecule is a linear function of the nuclear separation. Morse's potential function is not as general as a simple power series expansion of the potential function about the equilibrium point and so there has been some question as to what effect the difference between these forms for the potential function would have on the predicted intensities. It is the purpose of the present paper to compare the intensity formulas obtained from both potential functions and also to consider the effect on the intensities of higher terms in the power series expansion of the electric moment. Briefly stated the results are that the intensity formulas derived by the two methods give numerical results which differ by less than the experi-

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[2] J. L. Dunham, Phys. Rev. **34,** 438 (1929).

[3] P. M. Morse, Phys. Rev. **34,** 57 (1929).

mental error of the measurements, and that the inclusion of higher terms in the electric moment is, in general, necessary. The numerical agreement obtained previously does not have a unique interpretation. Either it is an indication that for HCl the coefficient of the quadratic term is very small indeed, or it is due to a cancellation of terms. The first part of the paper will deal with the derivation of the intensity formulas based on the two potential functions and with a comparison of these formulas; the second part will consider their application to the numerical results for HCl.

PART I

The ratio of the intensities of two corresponding lines in different bands has been shown to be[4]

$$\frac{\alpha_{nm}}{\alpha_{jk}} = \frac{\nu_{nm}}{\nu_{jk}}\left(\frac{P_{nm}}{P_{jk}}\right)^2 \tag{1}$$

where α_{nm} is the intensity of the line $n \rightarrow m$ and ν_{nm} is its frequency. P_{nm} is the matrix component of the electric moment associated with the line $n \rightarrow m$ and will hereafter be called the *intensity integral.* It is calculated from the expression

$$P_{nm} = \int p(r) R_n(r) R_m(r) dr \tag{2}$$

where $p(r)$ is the electric moment of the molecule and is a function of r, the nuclear separation, and $R(r)$ is the radial part of the wave function. If we expand $p(r)$ in a power series about the equilibrium point $(r = r_e)$ and change to the dimensionless variable $\xi = (r - r_e)/r_e$, we have

$$p(\xi) = p_e + p_e'\xi + \frac{p_e''}{2}\xi^2 + \frac{p_e'''}{6}\xi^3 + \cdots \tag{3}$$

where $p_e' = (dp/d\xi)_{\xi=0}$ etc., and, correspondingly

$$P_{nm} = p_e'\xi_{nm} + \frac{p_e''}{2}\xi^2{}_{nm} + \frac{p_e'''}{6}\xi^3{}_{nm} + \cdots \tag{4}$$

where $\xi^i{}_{nm} = \int \xi^i R_n R_m r_e d\xi$, is the $(n\ m)^{\text{th}}$ component[5] of the matrix ξ^i.

The expansion of the potential function about the equilibrium point can be written as

$$U = \frac{h\omega_e}{2\theta^2}(\xi^2 + a_1\xi^3 + a_2\xi^4 + a_3\xi^5 + \cdots) \tag{5}$$

where ω_e is the frequency of a classical oscillation for very small amplitudes, $\theta^2 = h/4\pi^2\omega_e I_e \ll 1$, I_e is the moment of inertia of the molecule, and a_1, a_2 and a_3 are arbitrary constants which can be determined from the frequencies of the

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[4] This formula was given in reference 2, p. 448. The material for its derivation is given very concisely by E. C. Kemble, Phys. Rev. **25**, 1 (1925); where the only change to be made by the new quantum mechanics is that on p. 6. $\overline{M}^2$ is to be replaced by $P_{nm}{}^2$.

[5] This expansion of P_{nm} is not to be confused with the expansion of charge distribution into dipoles and multipoles. This entire analysis concerns only the dipole radiation.

lines.[6,7] The first term gives the potential of a simple harmonic oscillator, for which the wave functions are known, but the wave functions of the more general case must be calculated by perturbation methods. Fues[7] has calculated the energy levels by this method and has given a formula for evaluating all of the integrals required in the perturbation calculation so that the details of the analysis will not be reproduced here. Suffice it to say that the perturbed wave functions are calculated by straight forward application of perturbation methods and from them the intensity integrals are obtained by Eq. (4).

The intensity integrals for the fundamental and the first two harmonic bands are found to be

$$P_{01} = \frac{p_e'\theta}{(2)^{1/2}}\left[1 + \theta^2\left(\frac{11}{16}a_1^2 - \frac{3}{4}a_2 - \frac{5\rho'' a_1}{4}\right)\right] \tag{6}$$

$$\begin{aligned} P_{02} = \frac{p_e'\theta^2}{2(2)^{1/2}}\bigg[&(a_1 + \rho'') + \theta^2\left(\frac{243}{32}a_1^3 - \frac{111}{8}a_1a_2 + 5a_3\right. \\ &\left. + \rho''\left(\frac{3}{32}a_1^2 - \frac{15}{8}a_2\right) - \frac{3a_1\rho'''}{2}\right)\bigg] \end{aligned} \tag{7}$$

$$P_{03} = \frac{p_e'\theta^3(3)^{1/2}}{4}\left[\frac{3a_1^2 + 4a_2}{8} + a_1\rho'' + \frac{\rho'''}{3}\right] \tag{8}$$

where $\rho'' = p_e''/p_e'$ and $\rho''' = p_e'''/p_e'$. The formulas for P_{01} and P_{02} have been carried out to a second approximation, and the formula for P_{03} has been given to show how higher derivatives of p enter into the intensity integrals for higher harmonics. There are no reliable intensity measurements for any second harmonic bands so far as I am aware, and consequently P_{03} has been given only to a first approximation.

Mensing and Dennison[8] have obtained by perturbation methods similar to those used here a formula for the intensity ratio of the harmonic to the fundamental band based on the first terms of Eqs. (6) and (7) but omitting the term in ρ'', and Fues[9] has given formulas for the intensity integrals to a first approximation, using Kratzer's potential function, which are closely related to the first terms in Eqs. (6), (7) and (8), but omitting ρ'' and ρ'''. However, the fact that ρ'' enters into the first term of P_{02} in Eq. (7), and that both ρ''' and ρ'' enter into P_{03}, shows that in general these terms cannot be neglected even to a first approximation. Generalizing from the above equations it seems that for the band $(0\rightarrow n)$ it is necessary to consider at least the first n terms in Eq. (4).[10]

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

[7] E. Fues, Ann. d. Physik. **80**, 367 (1926).

[8] Note by D. M. Dennison at the end of a paper by Meyer and Levin, Phys. Rev. **34**, 44 (1929). L. Mensing, Zeits. f. Physik **36**, 814 (1926).

[9] E. Fues, Ann. d. Physik **81**, 281 (1926).

[10] The reason for this can be seen quite simply by considering the case of P_{02} in the following fashion. The wave functions are those of an harmonic oscillator made slightly asymmetrical by the anharmonicity of the potential function. The integrand of ξ_{02} is composed of

It turns out that because the expressions for P_{nm} are even or odd in θ, it is necessary to carry the perturbation process two steps farther for each new term in θ added to P_{nm}, a behavior very like that found by Fues for the energy levels.

The frequency ratios which are necessary to calculate the intensity ratios (see Eq. (1)) are given by $\nu_{02}/\nu_{01} \cong 2(1-x)$ and $\nu_{03}/\nu_{01} \cong 3$ and the formula for x (which is the coefficient of the quadratic term in the vibrational energy level formula) as given by Fues[7] or Kemble[6] is $x = 3h[5a_1^2/4 - a_2]/16\pi^2\omega_e I_e$ so that the intensity ratios are given by

$$\frac{\alpha_{02}}{\alpha_{01}} = \frac{\theta^2}{2}\left[(a_1+\rho'')^2 + \theta^2\left(\frac{103}{8}a_1^4 - \frac{51}{2}a_1^2a_2 + 10a_1a_3 + \rho''\left(\frac{53}{4}a_1^3 - 27a_1a_2 + 10a_3\right) + \rho''^2\left(\frac{23}{8}a_1^2 - \frac{3a_2}{2}\right) + \frac{5a_1\rho''^3}{2} - 3a_1^2\rho''' - 3a_1\rho''\rho'''\right)\right] \tag{9}$$

$$\frac{\alpha_{03}}{\alpha_{01}} = \frac{9}{8}\theta^4\left[\frac{3a_1^2+4a_2}{8} + a_1\rho'' + \frac{\rho'''}{3}\right]^2. \tag{10}$$

The derivation of the formulas for P_{01}, P_{02} and P_{03} using the wave functions derived by Morse[3] is similar to the calculation of P_{02} given in reference 2, with the exception that the terms in ρ'' and ρ''' require evaluation of integrals of the type $\int e^{-kx}x^{k-i-1}(\log x)^n dx$. This offers no difficulty as they can be obtained by $(n-1)$-fold differentiation with respect to i of the formula for the integral with $n=1$. Since we are using only small quantum numbers and since $k = 1/x \gg 1$ it is possible to expand the logarithms and radicals appearing in the expressions for P_{nm}[11] in terms of $1/k = x$. This simplifies these expressions considerably.

$$P_{01} = \frac{p_e'(x)^{1/2}}{ar_e}\left[1 + x\left(\frac{1}{2} + \frac{5\rho''}{2ar_e}\right)\right] \tag{11}$$

$$P_{02} = \frac{p_e'x}{ar_e(2)^{1/2}}\left[\left(1 - \frac{\rho''}{ar_e}\right) + x\left(\frac{3}{2} + \frac{2\rho''}{ar_e} - \frac{3\rho'''}{a^2r_e^2}\right)\right] \tag{12}$$

$$P_{03} = \frac{p_e'x^{3/2}}{ar_e}\left(\frac{2}{3}\right)^{1/2}\left[1 - \frac{3\rho''}{2ar_e} + \frac{\rho'''}{2a^2r_e^2}\right]. \tag{13}$$

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the product of two wave functions both of which are nearly even functions, and of ξ which is an odd function, so that the *integrand* as a whole is nearly odd. Consequently in the *integral* there is nearly complete cancellation, it being saved from vanishing only by the slight asymmetry of the wave functions. Now ξ is a first order small quantity to begin with, because for low quantum numbers the wave functions are appreciable only for a small range of ξ about $\xi=0$, so ξ_{02} is a second order small quantity. On the other hand the integrand of ξ_{02}^2 is nearly even, all three factors being nearly even, so that there is no cancellation, but, since ξ^2 is a second order small quantity, the value of ξ_{02}^2 is of the second order too, and therefore of the same order of magnitude as ξ_{02}.

[11] Unfortunately in reference 2, Eq. (13) was incorrectly printed. The factor $A_oA_2k^{k-3}$ should be replaced by $[(k-2)(k-5)/2a^2]^{1/2}$.

From these the intensity ratios can be calculated at once.

$$\frac{\alpha_{02}}{\alpha_{01}} = x\left[\left(1 - \frac{\rho''}{ar_e}\right)^2 + x\left(1 + \frac{4\rho''^2}{a^2r_e^2} - \frac{5\rho''^3}{a^3r_e^3} - \frac{6\rho'''}{a^2r_e^2} + \frac{6\rho''\rho'''}{a^3r_e^3}\right)\right] \tag{14}$$

$$\frac{\alpha_{03}}{\alpha_{01}} = 2x^2\left[1 - \frac{3\rho''}{2ar_e} + \frac{\rho'''}{2a^2r_e^2}\right] \cdot \tag{15}$$

We are now in a position to compare the intensity ratio formulas given by the perturbation method with those given by Morse. This is best done by expanding Morse's potential function in powers of ξ about $\xi = 0$ giving

$$U = Da^2r_e^2\left(\xi^2 - ar_e\xi^3 + \frac{7}{12}a^2r_e^2\xi^4 - \frac{1}{4}a^3r_e^3\xi^5\right) \cdot \tag{16}$$

There are only two assignable constants in this expression, D and a, whereas in Eq. (5) all the terms have arbitrary coefficients. That is to say there are certain relations connecting the coefficients of all the higher terms in Morse's potential with that of the first term. Now if we impose these relations on the coefficients a_1, a_2 and a_3 in Eqs. (9) and (10), we find that we get exactly Eqs. (14) and (15), so that any numerical differences in the values of intensities calculated by these two methods would be entirely due to slight differences between the potential functions assumed and not to any difference in the mathematical analysis. It has been pointed out by Fues[7,8] that since the harmonic oscillator has no continuous spectrum and since the perturbing terms in the energy go to infinity for large values of ξ, intensity calculations based on this perturbation procedure are not to be relied upon. The identity of the two analyses shown here, however, proves that for low quantum numbers and to the approximations used, the absence of a continuous spectrum in the perturbation analysis has no effect upon the intensities.

A word should be said about the relative accuracy of the two methods. Although for accurate calculations the perturbation method is more precise than Morse's, because the potential function assumed can be fitted to any given molecule more accurately, nevertheless, for first approximations Morse's formulas are to be preferred. The reason is that the first term in Eq. (9) takes into account only the first perturbing term in the potential function, whereas the first term in Eq. (14) contains contributions from higher terms in the potential function as well. In other words Morse's intensity formula converges the more rapidly of the two, so that its *first term* is a better approximation than that of the perturbation formula.[12] For HCl, the numerical difference between the two second approximations is considerably less than the experimental error of the observed intensities. For gases like CO and NO where x is materially smaller than for HCl, the difference is very small even for the first order terms.

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[12] Of course perturbation methods could be applied to Morse's wave functions to obtain a more accurate intensity formula, but there is no need of this here in view of the relatively large experimental error.

PART II

We are now ready to turn to a consideration of the numerical values for HCl. Unfortunately there are no accurate data on the intensities of vibration-rotation bands for any other diatomic molecule, as data from imperfectly resolved bands observed with only one tube length or only one pressure are not in the least reliable for intensity measurements.

I have measured the intensity of several lines in the harmonic band of HCl[2] and shown that the observed ratio of the intensity of that band to the intensity of the fundamental band as observed by Bourgin[13] is 0.0161. The probable error of this ratio depends on the probable error of the measured intensities of both bands. The probable error of the harmonic is given (reference 2, p. 445) as 6 percent and Bourgin gives 25 percent as the "precision limits" of his measurements. Interpreting "precision limits" as a figure which the true error is unlikely to exceed, or that there is, say, but one chance in ten of the true error being greater than 25 percent, the probable error for the fundamental turns out to be 10 percent.[14] The probable error of the ratio is given by the square-root of the sum of the squares of the separate errors,[14] which is 12 percent. Thus we have for the observed value of the intensity ratio

$$\frac{\alpha_{02}}{\alpha_{01}} = 0.0161 \pm 0.0019. \tag{17}$$

Dennison,[9] on the basis of observations of Meyer and Levin, has estimated the ratio of these intensities as 0.021 ± 0.004, which agrees, within the limits of error, with the value just given. Dennison's estimate, however, is based on the measurements of one or at most two tube-lengths and so cannot be considered to be as accurate as the value given in Eq. (17).

To compare this value with the theoretical expressions for intensity it is necessary to substitute in Eqs. (9) or (14) the values of the measurable constants of HCl. Meyer and Levin[9] have recently published the results of new measurements of the wave-lengths of the HCl bands under higher dispersion than had previously been obtained and Colby[15] has derived the values of the various molecular constants from their data. These values differ appreciably from the constants used in reference 2. They are:[16]

$$\begin{aligned} I_e &= 2.613 \times 10^{-40} \text{ gm cm}^2 & a &= 1.710 \\ \omega_e &= 2988.7 \text{ cm}^{-1} & a_1 &= -2.34 \\ x &= 0.01725 & a_2 &= 3.62 \\ r_e &= 1.276 \times 10^{-8} \text{ cm} & a_3 &= -2.60 \end{aligned}$$

$$\theta^2 = 0.00709$$

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

[14] R. T. Birge, Phys. Rev. Supp. **1**, 1 (1929), esp. p. 4.

[15] W. F. Colby, Phys. Rev. **34**, 53 (1929).

[16] The values given are obtained by averaging the results for the two isotope components which is sufficiently accurate for our purposes. The value of a_3 has been obtained by using the value of $a^3 r_e^3/4$ (i.e. the value of a_3 according to Morse's analysis, cf. Eq. (16)). a_3 is a small term occurring only in a second order correction so that a more precise evaluation is not necessary.

Substituting these values in Eqs. (9) and (14) we have:

$$\frac{\alpha_{02}}{\alpha_{01}} = (0.0194 - 0.0166\rho'' + 0.00355\rho''^2) \qquad \text{(Pert)} \qquad (18)$$
$$(-\,0.0015 + 0.0008\rho'' + 0.00026\rho''^2 - 0.000147\rho''^3 - 0.000414\rho''' + 0.000177\rho'''\rho''.)$$

$$\frac{\alpha_{02}}{\alpha_{01}} = (0.0173 - 0.0159\rho'' + 0.00364\rho''^2) \qquad \text{(Morse)} \qquad (19)$$
$$(+\,0.0003 + \qquad + 0.00025\rho''^2 - 0.000143\rho''^3 - 0.000376\rho''' + 0.000173\rho'''\rho'')$$

In Eqs. (18) and (19) the two terms in θ appearing in Eqs. (9) and (14) have been kept separate to show that the formula from Morse's analysis converges more rapidly than the other so that its first term may be considered a better approximation than that of Eq. (9). If the two terms are combined, it is easy to see that the difference between the two second approximations cannot be greater than 2 percent, as none of the major terms differ by more than that amount.

In these equations the only unknowns are ρ'' and ρ'''. Unfortunately we cannot evaluate both of these constants from one equation, as the method of successive approximations would not yield very significant results for ρ''' in view of the relatively large experimental error. Consequently we shall use only the first terms and solve only for ρ''. Now, as we have seen, if we are going to use only the first term, Eq. (19) is more accurate than Eq. (18) so that we shall use the former in calculating ρ'', which gives us:

$$\rho'' = \begin{matrix} 0.066 \pm 0.13 \\ 4.30 \pm 0.13 \end{matrix} \qquad (20)$$

there being two values because the first term of Eq. (19) is quadratic in ρ''. Now $p'' = p_e''/p_e'$ and, for a known value of p_e' determines p_e''. Using the value of p_e' found by Bourgin[13] ($p_e' = 1.06 \times 10^{-18}$ e.s.u.) we have for ρ_e''

$$p_e'' = \left.\begin{matrix} 0.070 \times 10^{-18} \\ 4.56 \times 10^{-18} \end{matrix}\right\} \text{e.s.u.} \qquad (21)$$

p_e'' is the coefficient of the quadratic term in the expansion of $p(\xi)$ about $\xi = 0$ and consequently is a measure of the "curvature" of the electric moment at that point.

The fact that one of the values of p_e'' is zero (within experimental error) shows why in my previous paper on this subject[2] a calculation of the intensity ratio assuming a linear electric moment gave results in good agreement with the observed value. This correspondence, however, cannot be used to show that p_e'' is negligible because we have just seen that a value of p_e'' which is a good sized positive quantity (a negative quantity if p_e' is negative) *also* gives the correct value for the intensity ratio, and there is no way, using only intensity data, to distinguish between these two values of p_e''.

A similar ambiguity arises in the case of p_e' where, because of the quadratic dependence of the intensity on the electric moment, it is not possible to determine the sign of p_e' from intensity measurements alone. This ambiguity in the sign of p_e' leads to a sort of double ambiguity in p_e'' because a change of sign of p_e' changes the sign of p_e'' as determined from Eq. (20). This, of course, does not affect that value of p_e'' which is practically zero, but the other greater value may apparently have either sign depending on that of p_e'.

It has always been assumed that the electric moment of HCl is linear and that p_e' is positive in the region about the equilibrium point. These were natural assumptions when HCl was supposed to dissociate into ions, but in recent years, it has been shown that HCl probably dissociates adiabatically into neutral atoms,[17] which means that at least for large values of r, the electric moment decreases with increasing nuclear separation. This surely means that the curvature of the electric moment is appreciable somewhere, and there is no reason why it should be negligible at the equilibrium point, so that we cannot rule out the larger value of p_e'' until there is more detailed information on the form of p as a function of r. As far as the sign of p_e' is concerned, it is probably positive. The position of the hydrogen nucleus when at equilibrium, is generally considered to be inside the M shell of the chlorine atom and so we may assume that its distorting influence on the chlorine atom, and consequently the electric moment of the molecule, is not at its greatest, and hence p is still increasing with r.[18] This is a very rough sort of reasoning but owing to our complete ignorance about the detailed processes responsible for setting up electric moments in molecules with atomic binding, it is the only sort of reasoning that we can apply to the data at present.

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[17] V. Kondratjew, Zeits. f. Physik **48,** 583 (1928); R. Samuel, Zeits. f. Physik **49,** 95 (1928); F. London, Zeits. f. Physik **46,** 455 (1928) esp. p. 472 et seq.; Franck und Kuhn, Zeits. f. Physik **43,** 164 (1927) esp. p. 169.

[18] Assuming that the electric moment at r_e is near its maximum and has a positive slope, the most probable value of p_e'' is the small one (nearly zero) because the other implies a large positive curvature which is impossible in the neighborhood of a maximum. However the assump ion that r_e is near the maximum is too questionable to warrant definite predictions and the whole matter may be complicated by subsidiary maxima in the electric moment for values of r less than r_{max}.