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THE APPLICATION OF THE CORRESPONDENCE PRINCIPLE TO DEGENERATE SYSTEMS AND THE RELATIVE INTENSITIES OF BAND LINES*

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ABSTRACT

Relative intensities of band lines of a diatomic molecule according to the correspondence principle.—This paper originated in an attempt to harmonize the Kratzer half integral quantum numbers, for which there is strong evidence, with the observed symmetry in the intensities of the two branches of the HCl band at 3.46μ. First the infra-red spectrum of non-gyroscopic diatomic molecules is calculated, *treating the molecule as a degenerate system* with but one quantum condition for two degrees of freedom, following the detailed rules proposed by Kramers. This leads to a formula for the relative intensities of the lines in the two branches of the band which is unsymmetrical and disagrees with the experimental observations. The theoretical intensity (i.e. integral absorption coefficient) of the first line of the positive branch is more than twice that of the first line of the negative branch. This dissymmetry may be greatly reduced if the a priori probability of the upper quantum level, which appears as a factor in the intensity formula, is replaced by the mean of the a priori probabilities of the initial and final states. Such a modification of the theory is justified by a recalculation of intensities, *treating the molecule as a non-degenerate system*, e.g., one whose orbits are quantized in space under the influence of a weak magnetic field. A comparison between the theory and experiment involves the computation of the total absorptions to be expected in a tube of appreciable length using a relatively wide slit. If this computation is based on the assumption that the lines have no unresolved fine structure, the estimated absorptions do not agree with experiment, but the assumption that such a fine structure does exist, combined with the integral absorption coefficients of the modified theory, gives fair agreement with the available observations. *General theory of transition probabilities.* It is pointed out that the usual method of calculating probabilities involves a discontinuity in the intensities of spectrum lines when a degenerate system is converted into a non-degenerate one, as by a weak magnetic field. This seems improbable and the failure of the first calculation indicates that the usual rules for the treatment of degenerate systems require modification.

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* This article is essentially an expansion of a note published in the Proceedings of the National Academy of Science, 10, 274 (June 1924)

INTRODUCTION

THE characteristic feature of infra-red absorption bands on which Bjerrum based his well-known theory was the doublet structure as observed with a spectroscope of moderate resolving power. This structure, so similar to that to be expected on a purely classical basis from the compounding of molecular vibrations and rotations, is essentially an intensity distribution due, as Bjerrum supposed, to differences in the numbers of molecules effective in producing absorption in different parts of the band. The graph of the absorption coefficient plotted against frequency was concieved by him to be a doubled and somewhat distorted Maxwell distribution law curve for angular velocities. This hypothesis made possible the calculation of the molecular moments of inertia of diatomic gases from the spacing of the maxima of their absorption doublets. When the fine structure of the halogen hydride bands was discovered, it was assumed that the intensity of each component line was a measure of the number of molecules in the corresponding absorbing state and the theoretical relation between the doublet spacing of the gross structure and the molecular moment of inertia remained as before.[1] A comparison of the values of the moment of inertia of HCl obtained from the fine structure and from the gross structure gave one of the earliest important checks on the theory.

This simple view of the relative intensities of band components has been retained since the introduction of Bohr's hypotheses into band spectrum theory, but finally breaks down with the reinterpretation of the structure of the bands of the halogen hydrides in terms of half integral quantum numbers first suggested by Kratzer[2] and more recently confirmed by Colby.[3] In fact the writer in a paper read before the American Physical Society in April 1923,[4] opposed the application of the "half quantum" idea to the bands in question because of its apparent conflict with the observed distribution of intensities among their components.

This conflict will be readily understood by reference to Figs. 1 and 2 which show the well-known absorption curve for the HCl band at 3.5μ as observed by Imes[5] and by Brinsmade and Kemble.[6] The high frequency (positive) branch is supposed to be due to molecules which

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[1] Cf. N. Bjerrum, Verh. d. Deutsch. Phys. Ges. **16**, 640 (1914);
E. C. Kemble, Phys. Rev. **8**, 689 (1916)

[2] A. Kratzer, Münchener Akad. p. 107 (1922)

[3] W. Colby, Astrophys. J. **58**, 303 (1923)

[4] E. C. Kemble, Phys. Rev. **21**, 713 (1923)

[5] E. S. Imes, Astrophys, J. **50**, 260 (1919)

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

pick up a unit of angular momentum as they absorb vibrational energy, while the low frequency (negative) branch is produced by molecules which drop a unit of angular momentum in the process of absorption. The numbers on the lines in Fig. 1 show the rotational quantum numbers assigned in Kratzer's earlier theory to the associated initial states. The approximate equality of corresponding components of the positive and negative branches fits very well with this assignment of quantum numbers and the hypothesis that the intensity of an absorption component depends primarily on the initial state. But according to Kratzer's new theory, corresponding components of the positive and negative branches have neither the same initial state nor the same final state and hence should not have equal intensities. To be explicit, let us introduce the symbol (n, m) to denote the state of a molecule having the vibrational quantum number n and the nuclear angular momentum $mh/2\pi$. The first component of the positive branch is attributed by the new theory to the jump $(0, \frac{1}{2}) \rightarrow (1, 3/2)$, while the first component of the negative branch is supposed to result from the jump $(0, 3/2) \rightarrow (1, \frac{1}{2})$. The a priori probability of the initial state for the former of these two lines is half that for the latter and it can readily be shown that the number of molecules in it is not much more than half as great. In the writer's opinion the evidence from the combination principle brought forward by Colby in favor of the new assignment of quantum numbers is conclusive. We are therefore confronted with a sharp disagreement between the early simple theory of intensities and the experimental observations shown in Figs. 1 and 2.

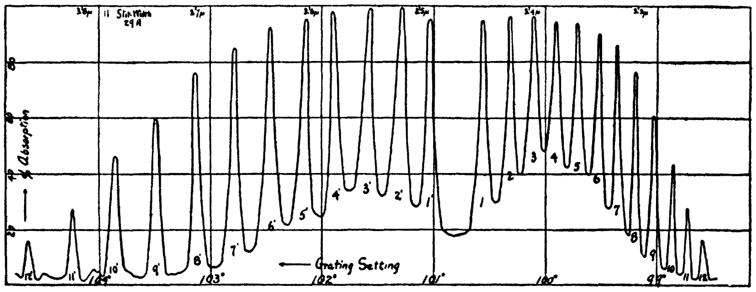

Fig. 1. The HCl band at 3.46μ, mapped with 7500-line grating; HCl at atmospheric pressure (Imes, Astrophysical Journal, **50**, 260, 1919).

The same difficulty is met in the study of electronic emission bands.[7] For example, the first components of the positive and negative branches

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[7] The writer is indebted to Prof. R. T. Birge for information on this point.

of the "cyanogen" band λ3383 A are of approximately equal intensity though neither the inital nor final rotational quantum numbers are the same for these two lines. Moreover, it follows from Kirchhoff's law that if the intensities of two absorption lines are proportional to the a priori probabilities of the initial states, the intensities of the same lines in emission must be proportional to the a priori probabilities of the corresponding final states—a conclusion of an unsatisfactory character.

The purpose of this paper is to study the problem from the standpoint of Bohr's correspondence principle. In the first part of the paper the intensities of the lines in the infra-red absorption spectrum of a diatomic gas will be calculated theoretically treating the molecule in the usual way as a degenerate system with but one quantum condition for two rotational degrees of freedom. The computed intensities are neither proportional to the numbers of molecules in the initial states[8] nor are they in agreement with the experimental observations. In the second part of the paper the intensities are recomputed assuming the existence of a slight precessional motion of the planes of rotation about the lines of the earth's magnetic field and space quantization of these planes. The recomputed intensities are in fair agree-

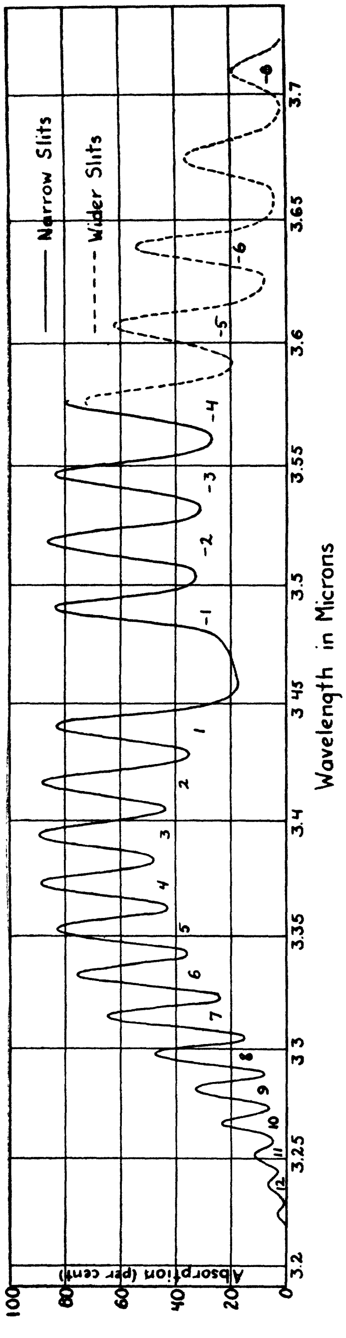

Fig. 2.

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[8] Contrary to the writer's earlier statement.[4]

ment with the experimental facts. In the writer's opinion the neutralization of the earth's magnetic field would probably not produce any great change in the actual relative intensities of the lines, so that the success of the second calculation is not to be interpreted as a proof of the reality of the assumed space quantization but points to the necessity of modifying the usual method of applying the correspondence principle to degenerate systems.

General Theory of the Intensities of Absorption Lines

Consider the absorption line due to jumps from the initial state (n'', m'') to the final state (n', m'). (The double prime will always denote the state of lower energy whether the discussion relates to absorption or emission.) Let N'' be the number of molecules in the initial state. Let u_ν denote the volume density of the radiant energy of frequency ν in the radiation field. In his basic derivation of the black body radiation formula Einstein treats u_ν as constant across the absorption line and sets the energy absorbed per unit volume per unit time equal to

$$N''B''_{\prime}u_\nu h\nu. \tag{1}$$

$B''_{\prime}$ denotes a numerical coefficient which gives the probability that any individual molecule in the initial state will make the transition in a unit time, and h is Planck's constant. If the symbol α_ν is introduced for the coefficient of absorption of the gas for light of frequency ν, the rate of absorption of energy per unit volume is readily shown to be

$$cu_\nu \int \alpha_\nu d\nu \tag{2}$$

where c is the velocity of light and the integration is carried over the width of the absorption line. It is convenient to introduce the symbol $\alpha''_{\prime}$ for the integral absorption coefficient $\int \alpha_\nu d\nu$. (This quantity is to be identified with the rather vague term "intensity of an absorption line" used in the introduction.) Equating the expressions (1) and (2) and solving for $\alpha''_{\prime}$ we get the fundamental relation

$$\alpha''_{\prime} = (h\nu/c)N''B''_{\prime}. \tag{3}$$

If the intensity of the beam of radiation used in the absorption measurements is not so great as to affect appreciably the relative numbers of molecules in the stationary states, we may introduce the usual statistical formula for N'' in terms of the temperature T, the energy W'', and the a priori probability p''. Eq. (3) takes the form

$$\alpha''_{\prime} = C\nu p'' e^{-W''/kT} B''_{\prime} \tag{4}$$

in which C depends only on the temperature and the nature of the gas.

Einstein[9] has shown that $B_{\prime}^{\prime\prime}$ is related to the probability coefficient $A'_{\prime\prime}$ for emission by spontaneous transition from the state (n', m') to the state (n'', m'') by the formula

$$B_{\prime}^{\prime\prime} = \frac{c^3}{8\pi h\nu^3} \; \frac{p'A'_{\prime\prime}}{p''} \; . \tag{5}$$

The expression for the integral absorption coefficient in terms of $A_{\prime\prime}$ is therefore

$$\alpha_{\prime}^{\prime\prime} = (C_1 p'/\nu^2) e^{-W''/kT} A'_{\prime\prime} \, . \tag{6}$$

APPLICATION OF BOHR'S CORRESPONDENCE PRINCIPLE: SYSTEM TREATED AS DEGENERATE.

In order to determine $A'_{\prime\prime}$ and $\alpha_{\prime}'$ theoretically, we use Bohr's correspondence principle. Let M_x, M_y, M_z denote the directional components of the electric moment of the molecule. Let X, Y, Z denote the respective amplitudes of the Fourier series components of M_x, M_y, M_z correlated in the usual way with the transition or "jump" which gives rise to the absorption and emission line under discussion. Each of these amplitudes depends on the particular "orbit" or motion for which it is worked out. The choice of orbit actually under consideration is conveniently indicated by its quantum numbers n and m. (In order to include in the discussion hypothetical non-quantized orbits between the initial and final states, it is convenient to define each of the quantum numbers as $1/h$ times the corresponding phase integral whatever its value may be). X, Y, Z are then functions of n and m. According to Kramers[10]

$$A_{\prime\prime} = (16\pi^4\nu^3/3hc^3) \, \overline{(X^2+Y^2+Z^2)}, \tag{7}$$

where the sum of the squares of the amplitudes is to be averaged over the hypothetical classical orbits between the initial and final states of the molecule. The method of averaging is uncertain, and, in fact, it is uncertain whether any definite scheme of averaging will always give rigorous results. Kramers has used the simple approximate assumption that X^2 is equal to the mean of the values of X^2 for the initial and final orbits. Other possibilities have recently been discussed by Hoyt.[11] The method of averaging is not important for the present purpose since the

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[9] A. Einstein, Phys. Zeits. **18**, 121 (1917)

[10] H. A. Kramers, Kgl. Danske Vidensk Selsk. Skrifter 8, Raekke III, 330 (1919). See also reference 11, equation (1).

[11] F. C. Hoyt, Phil. Mag. **47**, 826 (1924)

amplitudes are not greatly affected by a small change in m and since the variation of amplitude with the vibrational quantum number n does not affect the relative intensities of the lines in any single band. (We shall not attempt to discuss the relative intensities of the different bands in a system.) It has therefore seemed permissible to identify the mean values of X^2, Y^2, Z^2 with the values of these quantities for the intermediate orbit n,m whose quantum numbers are the averages of the values of n and m for the actual initial and final orbits. Using this assumption we rewrite (6) as follows:

$$a_{\prime}^{\prime\prime}=C_2\nu p^{\prime}e^{-W^{\prime\prime}/kT}\left[X^2(\bar{n}\,,\,\bar{m})+Y^2(\bar{n}\,,\,\bar{m})+Z^2(\bar{n}\,,\,\bar{m})\right]\,. \tag{8}$$

The electric moment of the molecule is assumed to be proportional to the vector distance between the atomic nuclei. Neglecting for the present any possible precession about lines of magnetic force and assuming a non-gyroscopic molecular model, it is clear that the motion of the terminal point of the vector M must be uniplanar and compounded of a vibration whose frequency we denote by ω_v and a rotation whose frequency we denote by ω_r. To determine X, Y, and Z we have to resolve M into components along three fixed axes and then analyze each component into Fourier series. The analysis is similar to that given by Sommerfeld and Heisenberg in their article on "The Intensity of Multiple Lines and their Zeeman Components."[12] It is convenient to introduce two sets of axes x, y, z and x', y', z' with a common origin. The first set is fixed in space, the xy plane being the plane of the orbit. The z' axis of the second set coincides with the z axis of the first and the $x'y'$ plane coincides with the xy plane, but the $x'y'$ axes rotate with constant angular velocity $2\pi\omega_r$ about the z axis. The sense of this rotation being the same as that of the molecule, it is evident that the orbit of the terminal point of M referred to the $x'y'$ axes is closed and periodic. If the molecular rotation took place at a uniform rate, the orbit would degenerate into a straight radial line, but owing to the variation in angular velocity with the radial vibrations of the molecule, it is actually of an elongated oval form as indicated in Fig. 3. Since the angular velocity of the molecule has its greatest value when the atoms are closest together, it is clear that the sense of the precession of the x' y' axes is opposite to the sense of rotation on the closed orbit in the x' y' plane.

The Fourier development is conveniently written in the complex form

$$M_{x'}+iM_{y'}=\sum_{\tau=0}^{\tau=\infty}\left[R_\tau e^{2\pi i(\tau\omega_v t+\delta)}+R_\tau^{\prime}e^{-2\pi i(\tau\omega_v t-\delta)}\right]\cdot\;\tau=0,\;1,\;2,\;\ldots \tag{9}$$

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[12] A. Sommerfeld and W. Heisenberg, Zeits. f. Phys. **11,** 131 (1922)

R^τ, $R^{\tau\prime}$, and δ denote real constants. Shifting to fixed axes is equivalent to multiplying by $e^{2\pi i\omega_r t}$ so that

$$M_x+iM_y=\sum_{\tau=0}^{\tau=\infty}\left[R_\tau e^{2\pi i[(\tau\omega_v+\omega_r)t+\delta]}+R'_\tau e^{-2\pi i[(\tau\omega_v-\omega_r)t-\delta]}\right]\cdot\ \tau=0,1,2,\qquad(10)$$

Each of the infra-red absorption bands of a diatomic gas is correlated with some particular value of τ. The positive branch of the band is associated with the classical Fourier component whose frequency is $\tau\omega_v+\omega_r$ while the negative branch is associated with the component of frequency $\tau\omega_v-\omega_r$. The relative probabilities of the transitions which give rise to the positive and negative branches of the band are therefore bound up with the relative values of R_τ and R_τ' respectively. The ratio of these coefficients depends in turn on the eccentricity of the orbit in the $x'y'$ plane. If this orbit is treated in first approximation as a radial straight line, these coefficients are equal. An exact determination of their values would be difficult and would require a specific assumption regarding the law of force governing the radial vibrations of the molecule. Without such an assumption, however, a second approximation valid for the coefficients R_τ and R_τ' of the important "fundamental" vibration-rotation band[13] may be carried through. It leads to the formulas

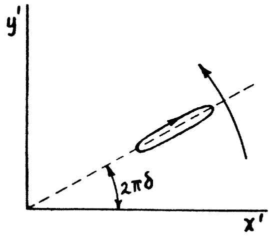

Fig. 3.

$$R_1=A\left(\frac{\omega_v}{\omega_v+\omega_r}\right)^2;\qquad R_1'=A\left(\frac{\omega_v}{\omega_v-\omega_r}\right)^2.\qquad(11)$$

The proof of these equations is given in the supplement to this paper. Further approximations hardly seemed justified at present. The amplitude A and the frequency ω_v in the above formulas vary slightly with the rotational quantum number of the orbit for which they are evaluated, but the variations in these quantities may be neglected in comparison with the large variations in ω_r.

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[13] See Supplementary Note at end of this paper.

It follows from the correspondence principle and Eq. (10) that R_τ and R_τ' are the amplitudes of the Fourier components of M_x and M_y corresponding to the transition groups for which $\Delta n=\tau$, $\Delta m=+1$, and $\Delta n=\tau$, $\Delta m=-1$, respectively.[14] The frequency ν absorbed in any given transition of the former class (positive branch) is the mean value of $\tau\omega_v+\omega_r$ taken over all orbits between the initial and final states, while the frequency absorbed in any given transition of the latter class (negative branch) is the corresponding mean value of $\tau\omega_v-\omega_r$. Hence Eqs. (11), translated into the notation of Eqs. (7) and (8), yield

$$X_1=Y_1=\text{Const.}/\nu^2; \qquad Z_1=0. \tag{12}$$

Eq. (8) specialized for the "fundamental" vibration-rotation band now becomes

$$\alpha_{\prime}^{\prime\prime}=\text{Const.}(p'/\nu^3)e^{-W''/kT}. \tag{13}$$

The approximations involved in Eqs. (12) and (13) are based on the assumption that ω_r is small compared with ω_v. This assumption is least accurate for the outer members of the band and Eq. (13) should be applied to them with caution.

COMPARISON OF THEORY AND EXPERIMENT

The above equation gives the relative intensities of the various components of the fundamental vibration-rotation band as required by the Bohr correspondence principle in the form hitherto accepted. It asserts that the relative intensity of any line is fixed by the product of three factors of which one is determined by the position of the line in the spectrum, another depends on the final state of the absorbing molecule (upper energy level), while the third depends on the initial state. The first factor $1/\nu^3$, due to the ellipticity of the orbit when referred to the rotating $x'y'$ axes, tends to make the outer components of the negative branch more intense than those of the positive branch. In the case of the HCl band shown in Figs. 1 and 2 the values of $1/\nu^3$ for the outermost components (+12 and −12) differ by about fifty per cent. This factor is of little importance in fixing the ratio of the intensities of neighboring lines. The second factor p' is the a priori probability of the upper energy level and is probably equal to $2m'+1$.[15] This factor tends to make the outer

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[14] Δn and Δm denote the increments in n and m respectively for the absorption process.

[15] Specific heat calculations for H_2 using the old integral rotational quantum numbers favor the use of the formula $p_m=2m$ (see Kemble and Van Vleck, Phys. Rev. **21**, 657-659, 1923), but the computations of R. C. Tolman (Phys. Rev. **22**, 470, 1923) based on half-integral quantum numbers favor the formula $p_m=2m+1$. The latter formula

components of both branches more intense than the inner ones. The exponential factor works in just the opposite way to p'. Fig. 4, Curve a, shows diagrammatically the integral absorption coefficients of the lines in the HCl band at 3.46μ as computed by Eq. (13) assuming

$$p'=2m'+1 \qquad m'=\tfrac{1}{2},\tfrac{3}{2},\tfrac{5}{2},\ldots \tag{14}$$

The values of w'' were computed from the formula

$$W''=10.46hc(m'')^2 \qquad m''=\tfrac{1}{2},\tfrac{3}{2},\tfrac{5}{2},\ldots$$

which is based on Colby's frequency measurements. The temperature of the gas in this and later computations is taken to be 293°K.

Curve b of Fig. 4 shows the effect on the computed intensities of arbitrarily replacing the factor p' by p'', thus making the absorption proportional to the number of molecules in the initial state.

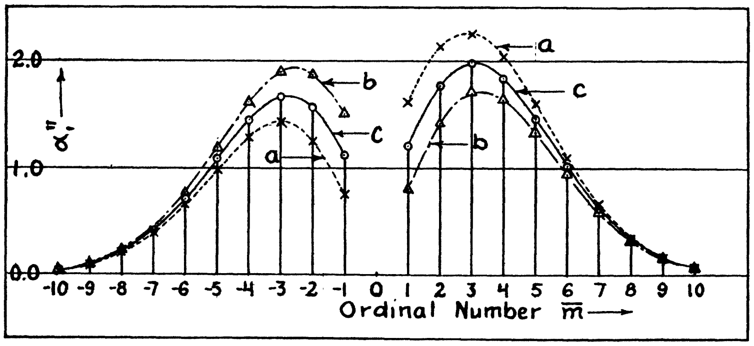

Fig. 4.

In comparing these graphs with the experimental curves of Figs. 1 and 2 the reader should bear in mind that the latter show total absorptions and not absorption coefficients, so that the intensity differences in them are to a large extent "ironed out." The differences between the two experimental curves, due largely to differences in slit width and tube length, are so considerable that close agreement with the theoretical curves is not to be expected. There is a marked discrepancy at the center of the band, however, which clearly shows that neither theoretical curve can be right. In curve a the high frequency branch is relatively much more intense than the low frequency branch, especially near the center, while in curve b the difference is reversed. In the measurements of Brinsmade and Kemble (Fig. 2) particular care was taken to observe

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is in accord with Heisenberg's assumption that the magnetic quantum numbers for "doublet" atoms should have the values ± (1/2, 3/2, 5/2, ...) (see W. Heisenberg, Zeits. f. Phys. **8**, 273 (1922).

the relative heights of the first maxima to the right and left of the center. They were very nearly equal, so that the experimental data are incompatible with both theories.

Remarks on the General Problem of Emission and Absorption by a Degenerate Molecular System

In view of the above discrepancy it is appropriate to re-examine the general problem of the intensities of absorption and emission lines in a degenerate system where the a priori probabilities of the initial and final states are not necessarily the same. Such a degenerate system, as is well known, may frequently be reduced to a non-degenerate one by the application of an external force field which resolves each of the original stationary states into a group of subsidiary states. The subsidiary states are equally probable and the number of such states in each group is equal to the a priori probability of the initial stationary state. In this case each of the original spectrum lines is resolved into a group of closely spaced components the intensities of which are calculable in theory as before. The new computations are simpler, however, and perhaps more certain, since the a priori probabilities of the various states, being equal, drop out of consideration. It seems to the writer altogether probable that the sum of the intensities of the group of lines produced by the external field will continuously approach the intensity of the parent line as the field approaches zero. This assumption will be called the hypothesis of the continuity of intensities. It makes possible the calculation of the intensities of emission or absorption lines due to a degenerate system in a new indirect way. It is supported by the fact that according to the classical electromagnetic theory no sudden change in intensity would be produced by an incipient external field, and also by the result of the calculations of the next section, but it is in conflict with the formulation of the correspondence principle by Kramers.

In order to see just how this formula disagrees with the hypothesis of the continuity of intensities, let us consider the radiation emitted as a result of a transition between two degenerate states S' and S''. It requires that the rate of spontaneous emission of radiation be proportional to $\nu^4 N'\overline{(X^2+Y^2+Z^2)}$. If a small external field is applied so that the upper energy level S' is broken up into p' subsidiary levels and the lower level into p'' subsidiary levels the combined rate of spontaneous emission due to all transitions from the upper group to the lower group is proportional to an expression of the form $\Sigma(k=1$ to $p_1')$ $\Sigma(l=1$ to $p'')$ $\nu_{kl}^4 N_k\ \overline{(X_{kl}^2+Y_{kl}^2+Z_{kl}^2)}$. Hence the hypothesis of the continuity of the intensities can harmonize with Kramers' theory only if, in the limit when the field is very small,

$$\nu^4 N' \overline{(X^2+Y^2+Z^2)} = \sum_{k=1}^{k=p'} \sum_{l=1}^{l=p''} \nu^4_{kl} N_k \overline{(X^2_{kl}+Y^2_{kl}+Z^2_{kl})} \,. \tag{15}$$

Introducing the statistical formulas for N' and the various N_k's and cancelling common factors, we reduce the above equation to the form

$$p' \overline{(X^2+Y^2+Z^2)} = \sum_{k=1}^{k=p'} \sum_{l=1}^{l=p''} \overline{(X^2_{kl}+Y^2_{kl}+Z^2_{kl})} \,. \tag{16}$$

The right hand member of (16) is symmetrically related to the a priori probabilities p' and p'' of the initial and final states, while the left hand member is unsymmetrical. The equation therefore must be incorrect, and either the assumption of continuous intensities or Eq. (7) must be given up.* In the next section we proceed to a recalculation of the relative intensities of band lines based on Kramers' theory for non-degenerate systems and on the hypothesis of the continuity of intensities.

Application of Bohr Correspondence Principle: System treated as Non-Degenerate

If the resultant intensity of a group of related lines produced by a small external field is sensibly the same as that of the single line into which they merge when the field is absent, it is clear that the resultant intensity must be independent of the exact nature of the external field and of the manner in which the degenerate system is made non-degenerate. In the absence of a satisfactory theory of the Zeeman effect for bands it seems plausible, therefore, to proceed with a formal application of the method of "spatial quantization" used in the theory of the Zeeman effect for hydrogen atoms. We assume that the component of the angular momentum parallel to the field is $rh/2\pi$, where r is the magnetic quantum number. We further

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* Note added at time of reading proof: Since writing this paper the author's attention has been called to the fact that in his dissertation[10] Kramers observed the existence of a discrepancy in the intensities of the fine structure components of the H and He$^+$ lines (a) computed directly, treating the system as degenerate, and (b) computed indirectly from the Zeeman analysis. He did not follow up the point, however, nor did he indicate which method was to be preferred.

Kramers also compared the intensities of the fine structure lines in the spectrum of He with the values of the product of a priori probability and square of amplitude worked out for the final state as well as the initial, thus showing that he clearly recognized the possibility that the a priori probability of the final state might have an influence on the probability of transition.

suppose that for any given m, r takes on the values $\pm 1/2, \pm 3/2, \ldots \pm m$.[16]

Associated with the magnetic quantum number r is a slight precessional motion of the orbital plane, of frequency σ. To get the new Fourier development the x, y, z system of axes previously considered may be supposed to rotate with constant angular velocity $2\pi\sigma$ about the lines of magnetic force. Let ξ, η, ζ be a new set of fixed axes so chosen that ζ coincides with the field. Let θ denote the constant angle between z and ζ. Without loss of generality we may assume that the x-axis lies in the ξ,η plane and makes an angle $2\pi\sigma t$ with the ξ axis. Shifting to the new axes we use the transformation equations

$$M_\xi + iM_\eta = \left\{ \tfrac{1}{2}(1+\cos\theta)\,(M_x + iM_y) + \tfrac{1}{2}(1-\cos\theta)(M_x - iM_y) \right\} e^{2\pi i\sigma t}\ ; \qquad (17)$$

$$M_\zeta = M_y \sin\theta\ .$$

Hence

$$\begin{aligned} M_\xi + iM_\eta = {} & \tfrac{1}{2}(1+\cos\theta)\left\{ Re^{2\pi i\left\{(\omega_v+\omega_r+\sigma)t+\delta\right\}} + R'e^{-2\pi i\left\{(\omega_v-\omega_r-\sigma)t-\delta\right\}} \right\} \\ & + \tfrac{1}{2}(1-\cos\theta)\left\{ Re^{-2\pi i\left\{(\omega_v+\omega_r-\sigma)t+\delta\right\}} + R'e^{2\pi i\left\{(\omega_v-\omega_r+\sigma)t-\delta\right\}} \right\} \qquad (18) \\ M_\zeta = {} & \sin\theta\left[R\sin\left\{2\pi(\omega_v+\omega_r)t+\delta\right\} - R'\sin\left\{2\pi(\omega_v-\omega_r)t-\delta\right\} \right] . \end{aligned}$$

The coefficients ± 1, 0 of ω_r and σ in the development give the values of Δm and Δr for the transitions with which the terms in the Fourier series are associated. Let $\Xi^{\Delta m}_{\Delta r}(\bar{m}, \bar{r})$, $\mathrm{H}^{\Delta m}_{\Delta r}(\bar{m}, \bar{r})$, $\mathrm{Z}^{\Delta m}_{\Delta r}(\bar{m}, \bar{r})$ be the ξ, η, ζ components of the amplitudes evaluated for the mean orbit $\bar{m}, \bar{r}$. Then, since $\cos\theta = r/m$,

$$\begin{aligned} & \Xi^{+1}_{+1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R(1+\bar{r}/\bar{m})\ ; \qquad \Xi^{+1}_{-1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R(1-\bar{r}/\bar{m})\ ; \\ & \Xi^{-1}_{+1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R'(1-\bar{r}/\bar{m})\ ; \qquad \Xi^{-1}_{-1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R'(1+\bar{r}/\bar{m})\ ; \\ & \mathrm{H}^{\Delta m}_{\Delta r}(\bar{m}, \bar{r}) = \Xi^{\Delta m}_{\Delta r}(\bar{m}, \bar{r})\ ; \qquad\qquad (19) \\ & \mathrm{Z}^{+1}_{0}(\bar{m}, \bar{r}) = R\sin\bar{\theta} = R\sqrt{1-(\bar{r}/\bar{m})^2}\ ; \quad \mathrm{Z}^{-1}_{0}(\bar{m}, \bar{r}) = R'\sqrt{1-(\bar{r}/\bar{m})^2} \end{aligned}$$

All other coefficients vanish.

---

[16] In accordance with Heisenberg's hypothesis as mentioned above[15].

The absorption intensity of one of the fine structure components is to be obtained from an equation of the form of (8) with p' set equal to unity and appropriate values of Ξ, H, Z replacing X, Y, Z. To get the total absorption intensity of a group of magnetic components we have to sum up over all values of $\bar{r}$ and Δr consistent with the values of $\overline{m}$ and Δm under consideration. As the discussion is restricted to a definite pair of values of n' and n'' and as ± 1 are the only values of Δm to be considered, it is convenient to modify the notation for the absorption coefficients. Let $\alpha^{+}(\overline{m})$ denote the integral absorption coefficient for the component of the high frequency branch ($\Delta m = +1$) having the mean rotational quantum number $\overline{m}$. Let $\alpha^{-}(\overline{m})$ denote the coefficient for the component of the negative branch having the same mean rotational quantum number. Then

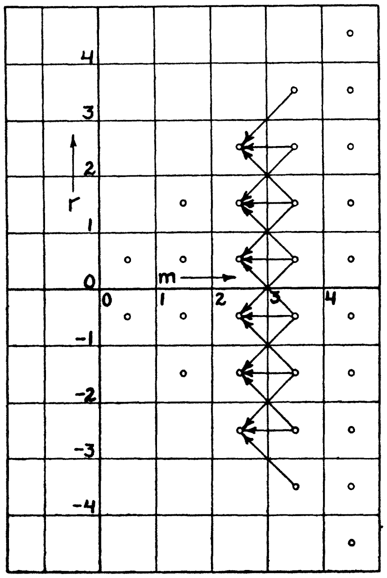

Fig. 5.

$$\alpha^{+}(\overline{m}) = \text{Const.} \times \nu R^2 \sum_{\bar{r}} \left\{ \tfrac{1}{2}(1+\bar{r}/\overline{m})^2 + \tfrac{1}{2}(1-\bar{r}/\overline{m})^2 + 1 - (\bar{r}/\overline{m})^2 \right\} e^{-W''/kT}$$

$$(20)$$

$$\alpha^{-}(\overline{m}) = \text{Const.} \times \nu R'^2 \sum_{\bar{r}} \left\{ \tfrac{1}{2}(1+\bar{r}/\overline{m})^2 + \tfrac{1}{2}(1-\bar{r}/\overline{m})^2 + 1 - (\bar{r}/\overline{m})^2 \right\} e^{-W''/kT}$$

Let $2S(\overline{m})$ denote the sum which appears in each of the above equations. Introducing the values previously obtained for R_1 and R_1' (thereby restricting the discussion as before to the fundamental band of the infra-red system) we condense (20) into the form

$$a^{\pm}(\bar{m}) = \text{Const.} \times [S(\bar{m})/\nu^3]e^{-W''/kT}. \tag{21}$$

In evaluating $S(\bar{m})$ it is convenient to make use of Fig. 5 in which r and m are laid out as ordinate and abscissa respectively. The circles indicate the r,m values of the assumed stationary states and the full arrows show a set of emission transitions giving rise to the third line in the positive branch of the band. The initial and final vibrational quantum numbers cannot be shown in two dimensions, but this incompleteness does not seriously detract from the value of the diagram.

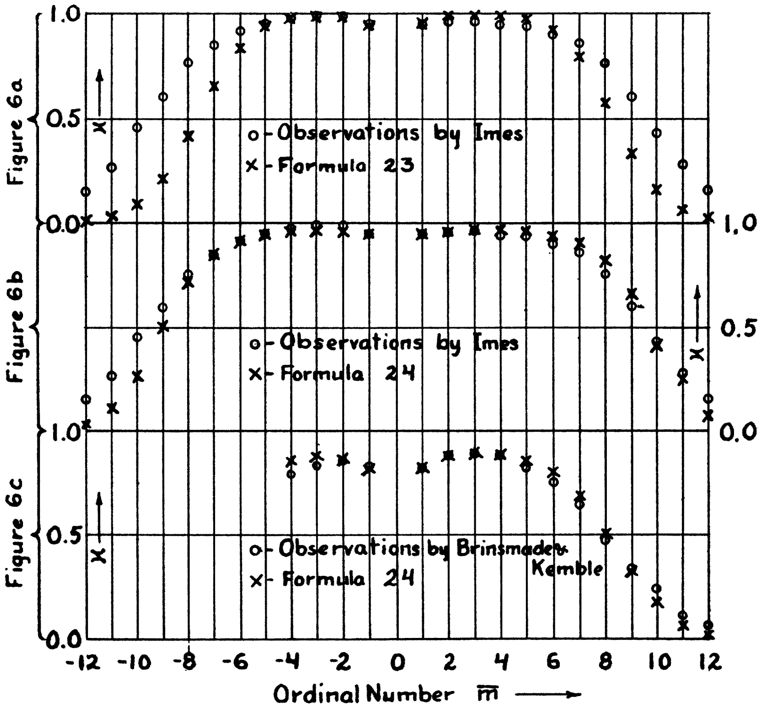

Fig. 6.

The subgroup of transitions for which $\Delta r = 0$ is shown by horizontal arrows. This subgroup gives rise to the term $[1-(\bar{r}/\bar{m})^2]$ in equations (20) and is to be summed from $\bar{r} = -(\bar{m}-\frac{1}{2})$ to $\bar{r} = +(\bar{m}-\frac{1}{2})$. The subgroup of transitions for which $\Delta r = +1$ is shown by downward pointing arrows (cf. note[14]). The term $\frac{1}{2}(1+\bar{r}/\bar{m})^2$ with which this second subgroup of transitions is correlated should be summed from $\bar{r} = -(\bar{m}-1)$

to $\bar{r}=\bar{m}$ according to the diagram, but since the added term is zero, we may formally sum from $-\bar{m}$ to $+\bar{m}$. Similarly the subgroup of transitions for which $\Delta r=-1$ yields the term $\frac{1}{2}(1-\bar{r}/\bar{m})^2$ which may be summed from $\bar{r}=-\bar{m}$ to $r=+\bar{m}$. Hence

$$2S(\bar{m})=\sum_{\tau=-\bar{m}}^{\tau=+\bar{m}}\left[1+(\tau/\bar{m})^2\right]+\sum_{\tau=-(\bar{m}-\frac{1}{2})}^{\tau=+(\bar{m}-\frac{1}{2})}\left[1-(\tau/\bar{m})^2\right]$$

$$=1+2\sum_{\tau=1}^{\bar{m}}\left[2+(\tau/\bar{m})^2-(\tau-\tfrac{1}{2}/\bar{m})^2\right].$$

A simple reduction yields the final formula

$$S(\bar{m})=2\bar{m}+1-1/4\bar{m}. \tag{22}$$

The number of subsidiary states in any group, i.e., $2m+1$, is equal to the a priori probability of the degenerate state from which the group is derived. The mean of the a priori probabilities of the initial and final degenerate states associated with any band line is $2\bar{m}+1$, so that $S(\bar{m})$ differs from the mean a priori probability only by the small term $1/4\bar{m}$. In view of the uncertainty of the method of averaging amplitudes on which (22) is based, it does not seem worth while to retain the term $1/4\bar{m}$ and therefore in the discussion of the agreement between the theory and experiment, $S(\bar{m})$ will be identified with the mean of the a priori probabilities of the initial and final states.

COMPARISON OF SECOND THEORY AND EXPERIMENT

Formula (21) differs from (13) only in the substitution of the mean a priori probability of the initial and final states for that of the final state. Curve *c* of Fig. 4 shows the relative integral absorption coefficients of the lines of the HCl band at 3.46μ as computed from (21). The intensities of the central components of the two branches are much more nearly the same, and, though the symmetry is less perfect than Fig. 1 would suggest, the discrepancies between the theory and experiment are much less serious than before.

In order to see more clearly just how important the discrepancies are, the writer has attempted to compute from the theoretical integral absorption coefficients a corresponding set of maximum total absorptions directly comparable with the absorption maxima of Figs. 1 and 2. Such a calculation is admittedly crude and serves merely to show that Eqs. (21) and (22) are not incompatible with the experimental data now available. The final test of the theory can only come after conclusive experimental measurements of the integral absorption coefficients have been made.

The computation of total absorptions is based on the assumption that the different lines are of the same breadth and structure so that the maximum absorption coefficients are in the same ratio as the integral absorption coefficients. A preliminary set of calculations was made on the hypothesis that the lines have no unresolved fine structure and that the radiation entering the slit of the receiving thermopile when set on the center of any individual line has a single definite absorption coefficient. The maximum observed fractional absorption, which we denote by the symbol κ, would then be given by a formula of the type

$$\kappa = 1 - e^{-a\alpha_{\prime}''} \tag{23}$$

TABLE I

Ordinal number $\overline{\mathrm{m}}$	$\alpha_{\prime}''$ (Eq. 21)	Maximum fractional total absorption κ (Eq. 23)	(Eq. 24)	Imes
+1	1.206	.950	.951	.948
−1	1.136	.941	.947	.950
+2	1.782	.988	.966	.958
−2	1.571	.980	.962	.992
+3	1.991	.993	.970	.961
−3	1.672	.984	.964	.990
+4	1.845	.990	.967	.945
−4	1.456	.973	.959	.976
+5	1.469	.974	.959	.940
−5	1.094	.934	.945	.951
+6	1.025	.922	.941	.900
−6	.718	.832	.916	.921
+7	.630	.791	.905	.858
−7	.415	.643	.856	.849
+8	.342	.573	.825	.763
−8	.212	.409	.725	.760
+9	.166	.338	.661	.605
−9	.097	.215	.505	.600
+10	.072	.164	.419	.433
−10	.040	.095	.270	.460
+11	.028	.068	.252	.280
−11	.0145	.035	.111	.273
+12	.010	.024	.074	.163
−12	.005	.012	.038	.156

in which a is a quantity the same for all the lines in the band but varying with the length of the absorption tube and the pressure of the absorbing gas. Table I and Fig. 6*a* show the result of the calculation. The circles in the figure show the experimental absorptions taken from Imes' curve and the crosses show the theoretical absorptions based on (23) after adjusting the constant a to give the best possible agreement for the central pair of lines. The marked discrepancies for the outer lines suggest that the exponential law of absorption does not apply. This result was anticipated in view of the doubling of the lines in the first harmonic band by the isotope effect.

A second set of calculations was therefore carried through on the hypothesis that the radiation entering the thermopile slit is uniformly distributed across a small frequency interval in which the coefficient of absorption a_ν varies linearly between zero and a maximum value ga_ν''. This assumption is merely a rough guess made to show in a general way the effect of an unresolved fine structure on the total absorption. If I_0 is the initial intensity of the beam of radiation and I the intensity after traversing a depth x of absorbing gas, we have

$$I = I_0 \int_0^{ga_\nu''} e^{-a_\nu x}\, da_\nu = I_0 \left(\frac{1 - e^{-ga_\nu'' x}}{ga_\nu'' x} \right).$$

The fractional total absorption is therefore

$$\kappa = \frac{I - I_0}{I_0} = 1 - \left(\frac{1 - e^{-aa_\nu''}}{aa_\nu''} \right), \tag{24}$$

where a is a new symbol for the product gx. The result of the calculation is shown in Table I and by Fig. 6b. As in Fig. 6a the circles show experimental values and the crosses the theoretical ones. Table II and Fig. 6c show the result of a similar attempt to fit the observations of Brinsmade and Kemble (Fig. 2) by means of formulas (21) and (24).

TABLE II

$\bar{m}$	κ (Eq. 24)	κ (Brinsmade and Kemble)
+1	.831	.825
−1	.822	.835
+2	.886	.884
−2	.870	.863
+3	.897	.891
−3	.878	.835
+4	.890	.886
−4	.860	.793
+5	.861	.826
−5	.814	
+6	.802	.756
−6	.724	
+7	.690	.647
−7	.572	
+8	.515	.474
−8	.379	
+9	.316	.330
−9		
+10	.158	.234
−10		
+11	.062	.280
−11		
+12	.020	.156

In view of the uncertainty regarding the relation between the fractional total absorption and the integral absorption coefficient and of the discrepancies between the two sets of observations shown in Figs. 1 and 2, the agreement between the computed values and the theoretical data seems to the writer fairly satisfactory. He is therefore of the opinion that the hypothesis of the continuity of intensities under the influence of a small perturbing field gives an acceptable way out of the impasse into which we are led by the direct application of equation (7) to the transitions of the degenerate diatomic molecule. The problem of reformulating a method of calculating the probabilities of transition for a degenerate system so as to conform to the new principle of continuity has yet to be solved.

REMARKS ON THE STRUCTURE OF THE LINES OF THE HCL INFRA-RED BANDS

The theory developed above had its origin in an attempt to harmonize the Kratzer half integral quantum numbers with the observed symmetry in the intensities of the positive and negative branches of the HCl band at 3.46μ. A related source of difficulty to which the writer called attention in the paper cited above[4] arises from the fact that according to Kratzer all of the lines except the pair adjacent to the center should be close doublets. His theory assumes that the electrons in such a diatomic molecule as that of HCl have a resultant angular momentum parallel to the nuclear angular momentum and directed either in the same or in the opposite sense. The magnitude of the electronic angular momentum is assumed to be such that the total angular momentum of the molecule is always an integral number of Bohr units. In this particular case (HCl) the electronic angular momentum is thought to be a half unit. The doublet structure of the band lines is a consequence of assigning slightly different energies to molecules having the same nuclear angular momentum but reversed directions for the electronic angular momentum. Ruling out all states for which the total angular momentum is zero then accounts for the absence of the "null" line at the center of the band and at the same time predicts that one component of each of the adjacent lines will be absent.

If this theory were correct, the intensities of the innermost lines of the two branches would not fit into a continuous series with the intensities of the other lines, but would be half as great as an extrapolation from the rest of the series would suggest. As a matter of fact the intensities of the lines in question show no such anomaly and we may conclude that their structure is the same as that of the other lines in the band.

The difficulty is not a serious one, however, for according to a modification of Kratzer's theory worked out by Kramers and Pauli the electronic angular momentum should always have the same sense as the nuclear angular momentum and the band lines should all be single. Some of the bands in the visible and ultra-violet region are made up of doublets which seem to bear out Kratzer's point of view while others are made up of single lines which fit better with the theory of Kramers and Pauli. The conclusion to be drawn from the intensities of the inner lines of the HCl band at 3.5μ is then simply that it belongs to the latter class.

SUPPLEMENTARY NOTE: PROOF OF FORMULAS (11)

The determination of the amplitudes in the formal Fourier development (9) involves the solution of the dynamical problem of the motion of the two atoms which make up the molecule. Let m_1 and m_2 denote the masses of the atoms, let ρ be the distance between the nuclei, and let $\varphi(\rho)$ be the net force of attraction. Then, as is well known, the dynamical problem reduces to that of a single particle of mass μ given by the formula $\mu = m_1m_2/(m_1+m_2)$ revolving about a fixed center of force under the influence of an attractive force $\varphi(\rho)$.

It is convenient to use the equations of motion of the particle referred to the rotating set of axes x', y' of Eq. (9). These are

$$\mu\frac{d^2x'}{dt^2} = -\frac{x'}{\rho}\phi(\rho)+\mu\omega_r^{\,2}x'+2\mu\omega_r\frac{dy'}{dt}\ ;$$

$$\mu\frac{d^2y'}{dt^2} = -\frac{y'}{\rho}\varphi(\rho)+\mu\omega_r^{\,2}y'-2\mu\omega_r\frac{dx'}{dt}\ .$$

The elimination of $\varphi(\rho)$ yields

$$x'\frac{d^2y'}{dt^2}-y'\frac{d^2x'}{dt^2} = -2\omega_r\left[x'\frac{dx'}{dt}+y'\frac{dy'}{dt}\right]. \tag{a}$$

This equation is immediately integrable, but it is convenient to use it as it stands, substituting for x' and y' their Fourier expansions and equating the coefficients of corresponding terms separately to each other.

We assume that x' and y' are proportional to M_x' and M_y'. Without loss of generality we may suppose that the x' axis coincides with the major axis of the orbit so that δ is equal to zero. The following equations are then easily derived from (9)

$$\begin{aligned} x' &= \Sigma\, a_\tau \cos 2\pi\tau\omega_v t,\ (\tau = 0 \text{ to } \infty) \\ y' &= \Sigma\, b_\tau \sin 2\pi\tau\omega_v t,\ (\tau = 0 \text{ to } \infty) \end{aligned} \tag{b}$$

where

$$a_\tau + b_\tau = aR_\tau;\quad a_\tau - b_\tau = aR_\tau'; \tag{c}$$

and α is a constant. For the present approximate investigation we may break off the series (b) after the terms for which $\tau=2$. Furthermore, as the motion is only slightly elliptical, we may simplify Eq. (a) by neglecting $y'\ dy'/dt$ in comparison with $x'\ dx'/dt$. The substitution of the initial terms of (b) into (a) then yields

$$b_1 = -2\frac{\omega_r}{\omega_v}a_1\left[1-\frac{a_2}{a_0}-\frac{3}{16}\ \frac{a_1^2}{a_0^2}\right], \tag{\textit{d}}$$

$$b_2 = -\frac{\omega_r}{\omega_v}a_2\left[1+\frac{a_1^2}{4a_0a_2}\right]. \tag{e}$$

The vibrational motion of a molecule having not more than one quantum of vibrational energy should be approximately simple harmonic so that a_2 should be small compared with a_1. As the vibrational amplitude is small compared with the mean distance between the nuclei a_0, it follows that the factor in brackets in Eq. (d) is not very different from unity. Combining (d) with (c), we then obtain

$$R_1=\frac{a_1}{\alpha}\left[1-2\frac{\omega_r}{\omega_v}\right]; \qquad R_1'=\frac{a_1}{\alpha}\left[1+\frac{2\,\omega_r}{\omega_v}\right].$$

Treating ω_r/ω_v as a small quantity, a further approximation yields

$$R_1=\frac{a_1}{\alpha}\left[\frac{\omega_v}{\omega_v+\omega_r}\right]^2; \qquad R_1'=\frac{a_1}{\alpha}\left[\frac{\omega_v}{\omega_v-\omega_r}\right]^2. \tag{\textit{f}}$$

These equations reduce to the form (11) when A is introduced as an abbreviation for a_1/α.

It remains to show that the variation in the product $A\,\omega_v^2$ or $a_1\omega_v^2$ may be neglected in comparison with that of $(\omega_v\pm\omega_r)^2$. The application to be considered has to do with the relative values of R_1 and R_1' worked out for a series of motions corresponding to the different lines in the fundamental rotation-vibration band. The vibrational quantum number for all these orbits is the same, viz., $n=\bar{n}=1/2$, while the rotational quantum number is equal to the ordinal number $(\bar{m})$ of the corresponding band line. The vibrational energy for a constant vibrational quantum number should be roughly proportional to the frequency of vibration as in the Planck linear oscillator. Hence the variation of the frequency ω_v with $\bar{m}$ is accompanied by a variation in the vibrational amplitude a_1 of such a character that to a first order approximation

$$a_1^2/\omega_v=\text{Const.},$$

or

$$a_1\omega_v \backsim \omega_v^{5/2}. \tag{g}$$

In order to estimate the relative variation of the factors $\omega_v^{5/2}$ and $(\omega_v \pm \omega_r)^2$ with $\overline{m}$ we make use of the theorem that the frequency of any spectrum line is equal to a suitable mean value of the corresponding classical frequency taken over a series of hypothetical orbits intermediate between the initial and final states. It follows from this theorem that the frequency of any line in the positive branch is

$$\nu^+(\overline{m}) = \overline{\omega}_v + \overline{\omega}_r, \tag{h}$$

while the frequency of a line in the negative branch is

$$\nu^-(\overline{m}) = \overline{\omega}_v - \overline{\omega}_r. \tag{i}$$

The mean frequencies $\overline{\omega}_v$ and $\overline{\omega}_r$ are nearly equal to the values of ω_v and ω_r for the intermediate orbit whose quantum numbers are $\overline{n}$ and $\overline{m}$. Hence we may eliminate $\overline{\omega}_r$ between (h) and (i) by using the frequencies of corresponding lines in the two branches. Thus

$$\omega_v(\overline{m}) = \tfrac{1}{2}[\nu^+(\overline{m}) + \nu^-(\overline{m})]. \tag{j}$$

The above formula permits the evaluation of ω_v from the spectroscopic frequencies of the band lines. In the case of the HCl band at 3.5μ, ω_v (1), the vibrational frequency associated with the central components of the band, is 1.4 per cent greater than ω_v (12) and $[\omega_v\ (1)]^{5/2}$ is 3.5 per cent greater than $[\omega_v\ (12)]^{5/2}$. On the other hand the value of $(\omega_v \pm \omega_r)^2$ for the 12th line of the positive branch (i.e. the square of the frequency of that line) is 41 per cent greater than the corresponding value for the 12th line of the negative branch. For this reason it seems permissible to treat $\omega_v^{5/2}$ and $a_1\omega_v^2$ as constant across the band in the present approximate calculations.

Jefferson Physical Laboratory,
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October 11, 1924.