THE BOHR THEORY AND THE APPROXIMATE HARMONICS IN THE INFRA-RED SPECTRA OF DIATOMIC GASES.

By Edwin C. Kemble.

Synopsis.

Infra-red spectra of diatomic gases; a quantum theory. The author's earlier theoretical *explanation of the occurrence of approximate harmonics* in the infra-red spectra of HCl, HBr and CO, based on the non-linearity of the law of force governing the relative displacement of the component atoms, encountered three difficulties: it did not explain the inexactness of the harmonics; it gave a wrong ratio for the asymmetry constants of the fundamental and harmonic bands; and it was in serious conflict with Kirchhoff's law. It is now shown that by *adopting Bohr's hypotheses* that the molecules possess a series of discrete, non-radiating states of vibration and that the frequencies radiated and absorbed are determined by the energy emitted or absorbed, a new explanation is obtained which seems to overcome the difficulties mentioned above. In connection with the discussion the author presents a full account of his *theory of the asymmetry* of the bands, which postulates a decrease in the frequency of vibration of a rotating diatomic molecule with increasing angular velocity, a consequence of the non-linearity of the law of force. It is found that the theory gives the observed value of the ratio of the asymmetry constants only if it is assumed that the minimum kinetic energy for vibratory motion is not finite as for rotary motion in the Bohr theory, but is zero.

Kirchhoff's law; suggested limitation. The author's theory of the structure of these band spectra is based on a theory which involves a minor contradiction to Kirchhoff's law since it leads to the conclusion that the ratio of the intensities of any two component parts of an absorption band is independent of the temperature. This suggests that Kirchhoff's law may not hold in such cases.

Introduction.

In 1916 the writer published a theoretical paper[1] predicting the occurrence of weak harmonics to the principal absorption bands in the infra-red spectra of diatomic gases. The theory was based on the assumption that the form of the electromagnetic waves radiated or absorbed by an oscillating dipole must be related to the form of the vibration in the manner indicated by the classical electromagnetic theory. It was shown that, on account of the non-linearity of the law of force governing the relative displacement of the atoms of a diatomic molecule, vibrations of these atoms along their line of centers having the amplitudes called for by the quantum theory must depart considerably from the simple harmonic type. According to Fourier's theorem the

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[1] Phys. Rev. (Ser. 2), 8, 1916 (701).

radiation emitted from such a vibrator should therefore consist of a harmonic series of wave-lengths. It was assumed that the entire series of emitted frequencies must also be absorbed. The infra-red absorption bands of diatomic gases, which are believed to have their origin in the atomic vibrations under consideration, should accordingly be accompanied by faint harmonics. As an example of the occurrence of such faint harmonics, the infra-red absorption bands of carbon monoxide were cited at the time, while a later paper[1] by Dr. J. B. Brinsmade and the writer reported the discovery of similar harmonic absorption bands in the infra-red spectra of HCl and HBr, which were held to constitute a verification of the theory.

There were, however, three difficulties in connection with the above explanation of the observations, viz., (*a*) the fact that the observed harmonics seemed not to be exact, the wave-length of the center in each case being from 0.025 μ to 0.045 μ greater than its calculated value, (*b*) the fact that the relation between the assymmetry constants of the fundamental and harmonic absorption bands in the HCl spectrum was not that predicted by the theory, and (*c*) the incompatibility of the theory itself with Kirchhoff's law. In the absence of an alternative explanation of the phenomena, and in view of the inherent plausibility of the explanation given above, the writer was inclined to attribute the discrepancies (*a*) and (*b*) to a slight error of unknown origin in the dispersion curve for quartz used in calculating the wave-lengths, and to assume that these harmonics constitute a *bona fide* exception to Kirchhoff's law. He now desires to report that the hypotheses adopted by Bohr in his theory of radiation and of atomic structure afford an alternative explanation of the observed phenomena which seems to avoid the above-mentioned difficulties.

THE APPLICATION OF BOHR'S HYPOTHESES TO RADIATION FROM VIBRATING DIATOMIC MOLECULES.

We proceed to the application of Bohr's hypotheses to the radiation from a vibrating diatomic molecule. The molecules are assumed to possess a series of discrete, non-radiating, steady, possible states of vibration. Let τ denote the number of any of these steady states, and let W_τ denote the corresponding energy of vibration. The law of force governing the motion being nonlinear, the frequency of vibration, ω, will depend upon the energy and therefore upon τ. In accordance with the earlier form of Planck's theory we assume that the energy of vibration is always an integral multiple of $h\omega$. (See supplementary note). Thus

$$W_\tau = \tau h\omega, \qquad \tau = (0), 1, 2, 3, \cdots. \quad (1)$$

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

According to the Bohr theory the angular momentum of an electron attached to a single hydrogen atom cannot be reduced below the minimum value $h/2\pi$. The observed structure of the infra-red absorption bands of HCl indicates that the above remark is also true of the angular momentum of a diatomic molecule.[1] These considerations create the presumption that the energy of any vibratory degree of freedom as well as that of any rotational degree of freedom must always be greater than zero, in accordance with which zero should be eliminated from the list of the possible values of τ in the above equation. There is some evidence in the present theory, however, that such a generalization is incorrect, and the question will accordingly be left open.

With Bohr we add the hypothesis that the frequency of the radiation emitted or absorbed by the molecule in passing from the steady state τ_1 to the steady state τ_2 is given by the relation

$$h\nu = \left| (W_{\tau_2} - W_{\tau_1}) \right|. \tag{2}$$

Combining these assumptions, we obtain the following expression for the radiation frequencies emitted or absorbed:

$$\nu = \left| (\tau_2\omega_{\tau_2} - \tau_1\omega_{\tau_1}) \right|. \tag{3}$$

If the frequency of vibration were completely independent of the amplitude, as in the case of an ideal linear oscillator, the frequencies emitted and absorbed would all be integral multiples of ω. If the frequency of vibration is nearly independent of the amplitude, the frequencies of the radiation emitted and absorbed will be approximately integral multiples of the frequency of vibration for small amplitudes. This theory, therefore, like the other, predicts the occurrence of (approximate) harmonics, though it gives them a different interpretation. The fundamental absorption band is due to the molecules jumping from the first of the steady states of vibration to the second (at ordinary temperatures the number of molecules normally in the second steady state is infinitesimal), while the first harmonic is due to the molecules jumping from the first steady state to the third.

Let us now see how the present theory meets the difficulties encountered by the former.

Wave-lengths of "Harmonics."

The fact that the wave-length of the center of the "harmonic" band is in each case observed to be a little more than half of the wave-length of the fundamental fits perfectly with the new theory. We may assume as a first approximation for small amplitudes that the equation

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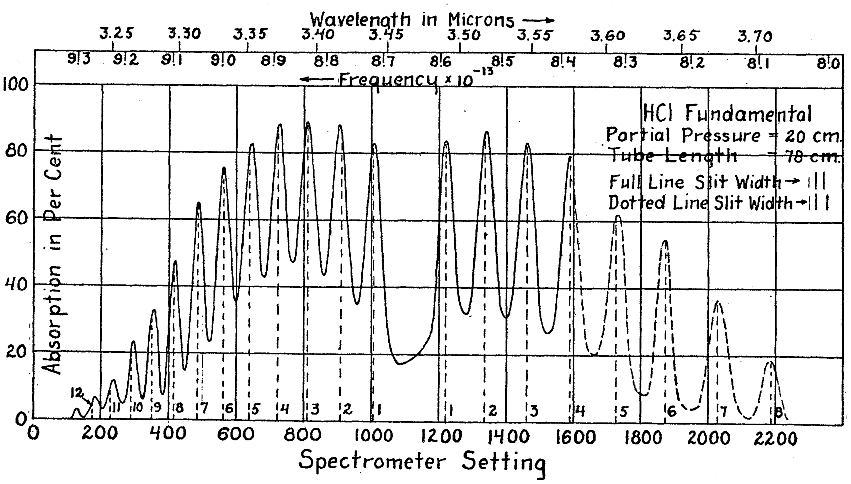
[1] Brinsmade and Kemble, l. c., p. 425.

of motion may be thrown into the form[1]

$$m\frac{d^2z}{dt^2} = -kz - k_2z^2. \tag{4}$$

In this case, whatever the sign of k_2, the frequency of vibration decreases when the amplitude increases.[4] Consequently the energy of a molecule should increase by a smaller amount when the molecule passes from the second steady state to the third than when it passes from the first to the second, and the frequency absorbed in passing from the first steady state to the third should be a little less than twice that absorbed in passing from the first to the second.

In order to show that the present theory is in qualitative agreement with the observed relative asymmetry of the two infra-red absorption bands of HCl it is necessary to indulge in some mathematical analysis. The writer has never published a full account of his theory of the asymmetry of the infra-red absorption bands of diatomic gases[2] and therefore welcomes this opportunity to present that theory in complete form.



THE ASYMMETRY OF THE INFRA-RED ABSORPTION BANDS OF DIATOMIC GASES.

According to the elementary theory of the structure of the infra-red absorption bands of diatomic gases given by Bjerrum[3] each of these

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[1] Reference No. 1, p. 708.

[2] The theory was first stated in an unpublished paper bearing the title "The Infra-red Absorption Bands of Gases and the Application of the Quantum Theory to Molecular Rotations" read before the American Physical Society on December 28, 1916. A brief statement of the essentials of the theory is to be found in the paper by Brinsmade and Kemble cited above.

[3] N. Bjerrum, Nernst Festschrift, Halle, 1912; Verh. d. D. Physik. Ges., 16, 1914 (640).

bands owes its width primarily to the effect of the molecular rotations and should be composed of a double series of elementary bands or quantum lines. (These elementary bands are themselves of quite appreciable breadth, but in order to distinguish them from the composite band which they unite to form, it will be convenient to designate them in the remainder of this paper as "quantum lines.") The molecules are assumed to vibrate with a common frequency ω. The radiation emitted and absorbed by the molecules which rotate with the frequency ν_r is divided between the frequencies $\omega + \nu_r$ and $\omega - \nu_r$. Consequently the molecules having any given angular velocity give rise to a pair of narrow absorption lines whose separation on the frequency scale is twice the frequency of the rotation. According to the quantum theory the frequencies of rotation must all be integral multiples of a certain basic frequency which we denote by the symbol ν_1. Hence the only frequencies radiated or absorbed are those given by the formula

$$\nu = \omega \pm p\nu_1, \qquad p = 1, 2, 3, \cdots. \quad (5)$$

Thus the quantum lines corresponding to different values of p should be equally spaced. Since the two absorption lines corresponding to each value of p are due to the same group of molecules, they should be of nearly equal intensity, while the intensities of the lines corresponding to different values of p should vary with the numbers of molecules in the corresponding groups. Consequently the large band of which these lines are the components should have the general appearance of a symmetrical doublet.

The accompanying figure shows the appearance of the principal band in the infra-red spectrum of HCl as observed by Dr. Brinsmade and the writer.[2] Instead of being equally spaced, the quantum lines are obviously closer together on the high frequency side and it is evident that if the band is observed with a spectrometer of low resolving power it will appear to be an asymmetric doublet, the high frequency maximum being the more intense. This group of lines and the approximately harmonic group in the same spectrum are the only infra-red absorption bands in the spectra of the diatomic gases which have been resolved into their elementary components, but the infra-red absorption bands of the other diatomic gases are similarly asymmetric doublets.

In the writer's opinion the asymmetry is due to a decrease in the frequency of vibration with increasing angular velocity. This decrease results from the nonlinearity of the law of force which governs the vibratory motion.

In order to reduce the above hypothesis to quantitative form, we proceed to formulate the equations of motion of the rotating and vibrating molecule. It will be assumed that the masses of the two atoms, m_1 and m_2, are concentrated in the nuclei. Let ζ denote the distance between the atomic centers and let

$$m = m_1 m_2/(m_1 + m_2).$$

Let θ denote the angle between the line of the atomic centers and any fixed line in the plane of the motion. With this notation the expression for the kinetic energy of the system is readily reduced to the form

$$T = \frac{m}{2}\left[\left(\frac{d\zeta}{dt}\right)^2 + \zeta^2\left(\frac{d\theta}{dt}\right)^2\right]. \tag{6}$$

Denoting the potential energy by $\Phi(\zeta)$ and setting up Lagrange's equations, we have

$$\frac{d}{dt}(m\dot{\zeta}) - m\zeta\dot{\theta}^2 + \Phi'(\zeta) = 0 \tag{7}$$

and

$$\frac{d}{dt}(m\zeta^2\dot{\theta}) = 0. \tag{8}$$

Equation (8) gives rise to the statement of the constancy of the angular momentum. This may be written

$$m\zeta^2\dot{\theta} = m\zeta_0{}^2\Omega_0, \tag{9}$$

where ζ_0 is assumed to be the distance between the nuclei when the molecule is in equilibrium and at rest, while Ω_0 is the angular velocity of the moving molecule when ζ passes through the value ζ_0. Substituting from (9) into (7) we obtain the differential equation for the vibratory motion:

$$m\frac{d^2\zeta}{dt^2} = -\Phi'(\zeta) + m\frac{\Omega_0{}^2\zeta_0{}^4}{\zeta^3}. \tag{10}$$

Let U denote the total energy of vibratory and rotational motion, and let ζ_1 and ζ_2 denote the minimum and maximum values of ζ. Integration of equation (10) then gives the following expression for the period of the vibration:

$$\tau = \sqrt{2m}\int_{\zeta_1}^{\zeta_2}\frac{d\zeta}{\sqrt{U - \Phi(\zeta) - \dfrac{m\Omega_0{}^2\zeta_0{}^4}{2\zeta^2}}}. \tag{11}$$

Obviously ζ_1 and ζ_2 are roots of the equation

$$U - \Phi(\zeta) - \frac{m\Omega_0{}^2\zeta_0{}^4}{2\zeta^2} = 0. \tag{12}$$

Ω_0 can be identified with the mean angular velocity of the molecule without appreciable error and equation (11) shows that the period of vibration is a function of Ω_0. It also shows that if τ, or its reciprocal, the frequency of vibration, ω, is expanded into a power series in Ω_0, the coefficients of the odd powers must vanish, since a reversal of the sign of Ω_0 cannot affect the value of τ. Denoting the frequency of rotation by $p\nu_1$ and the frequency of vibration for zero angular velocity by ω_0, we may therefore write as a first approximation

$$\omega = \omega_0 - ap^2\nu_1^2. \tag{13}$$

The coefficient a is a function of the total vibrational energy W. It will be shown later on that in general we may expect a to be positive.

If we adopt the fundamental hypothesis of the writer's earlier work, which identifies the frequency of vibration of the molecule with the mean of the two radiation frequencies absorbed (or radiated), and combine equations (5) and (13), we obtain

$$\nu = \omega_0 - ap^2\nu_1^2 \pm p\nu_1. \tag{14}$$

This is the equation for the position of the quantum lines given in the writer's former brief statement of the theory of asymmetry.[1] If the values of ω_0, a, and ν_1 are properly chosen, the formula gives the frequencies of the quantum lines in the HCl fundamental with considerable accuracy (cf. the vertical dashed lines in the figure[2]).

The positions of the lines in a true harmonic should be given by

$$\nu = 2(\omega_0 - ap^2\nu_1^2) \pm p\nu_1. \tag{14a}$$

Equation (14*a*) is of the same form as (14) and gives the frequencies of the quantum lines in the observed harmonic correctly if the values of the constants ω_0 and a are readjusted. No readjustment of the value of ν_1 is necessary.

Equation (5), however, does not fit with the fundamental hypotheses regarding the nature of the process of radiation on which the present paper is based. In order to bring the theory of asymmetry into line with the Bohr theory we must assume that equation (3) gives the mean of the two frequencies emitted and absorbed by any one group of molecules.[3] Confining our attention to the process of absorption, we replace equation (5) by

$$\nu = \tau_2\omega_{\tau_2} - \tau_1\omega_{\tau_1} \pm p\nu_1, \qquad \begin{cases} p = 1, 2, 3, \cdots, \\ \tau_2 > \tau_1. \end{cases} \tag{15}$$

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[1] Brinsmade and Kemble, l. c., p. 424.

[2] The consistent discrepancy in the outermost quantum lines on the high frequency side is completely eliminated without the introduction of fresh arbitrary constants if the change in the moment of inertia due to the expansion of the molecule with increasing angular velocity is taken into account.

[3] An equivalent assumption has been used by Bohr to explain the Zeemon effect. Cf. Phil. Mag., 27, 1914 (520).

Since the frequency of vibration depends on the angular velocity and on the energy of vibration, ω is to be regarded as a function of τ and p. Moreover, the constant a is a function of τ. We therefore introduce the notation

$$\omega \equiv \omega(\tau, p);$$

$$a \equiv a(\tau).$$

Equation (13) becomes

$$\omega(\tau, p) = \omega(\tau, 0) - a(\tau)p^2\nu_1^2. \tag{16}$$

Combining (15) and (16), we obtain

$$\begin{aligned} \nu = {} & \tau_2[\omega(\tau_2, 0) - a(\tau_2)p^2\nu_1^2] \\ & - \tau_1[\omega(\tau_1, 0) - a(\tau_1)p^2\nu_1^2] \pm p\nu_1. \end{aligned} \tag{17}$$

Let $N(\tau_1, \tau_2)$ and $\mathfrak{A}(\tau_1, \tau_2)$ be defined by the equations

$$\begin{aligned} N(\tau_1, \tau_2) &\equiv \tau_2\omega(\tau_2, 0) - \tau_1\omega(\tau_1, 0), \\ \mathfrak{A}(\tau_1, \tau_2) &\equiv \tau_2 a(\tau_2) - \tau_1 a(\tau_1). \end{aligned} \tag{18}$$

Then (17) becomes

$$\nu = N(\tau_1, \tau_2) - \mathfrak{A}(\tau_1, \tau_2)p^2\nu_1^2 \pm p\nu_1. \tag{19}$$

This equation is of the same form as (14) and consequently gives the positions of the lines in either of the HCl bands with equal accuracy.

The specific expressions for N and $\mathfrak{A}$ for the fundamental and first harmonic differ according as we assume that zero is or is not a possible value of τ. If it is not, $\tau_1 = 1$ and $\tau_2 = 2$ for the fundamental. Thus

$$\begin{aligned} N &= 2\omega(2, 0) - \omega(1, 0), \\ \mathfrak{A} &= 2a(2) - a(1). \end{aligned} \tag{20}$$

In the case of the first harmonic we should then have $\tau_1 = 1$ and $\tau_2 = 3$. Denoting the values of N and $\mathfrak{A}$ for the first harmonic by the symbols N' and $\mathfrak{A}'$, we obtain

$$\begin{aligned} N' &= 3\omega(3, 0) - \omega(1, 0), \\ \mathfrak{A}' &= 3a(3) - a(1). \end{aligned} \tag{21}$$

If, on the other hand, we adopt the alternative hypothesis that zero is a possible value of τ, the above equations become

$$\begin{aligned} N &= \omega(1, 0); \\ N' &= 2\omega(2, 0); \\ \mathfrak{A} &= a(1); \\ \mathfrak{A}' &= 2a(2). \end{aligned} \tag{22}$$

In either case, if a were independent of the energy of vibration, $\mathfrak{A}'$

would be equal to $2\mathfrak{A}$. This relation is the same as that called for by the old theory and does not agree with experiment, since the observed value of the ratio of the asymmetry constants $\mathfrak{A}'$ and $\mathfrak{A}$ is a little less than 1.5. On the other hand, if a decreases regularly as the energy of vibration increases, it is to be expected in either case that the ratio of $\mathfrak{A}'$ to $\mathfrak{A}$ will be less than 2.

In order to justify fully the present revised theory of the structure of these infra-red absorption bands, it would be necessary to derive the observed values of the constants N, N', $\mathfrak{A}$, and $\mathfrak{A}'$ on the basis of a plausible form for the potential energy function Φ. Mathematical difficulties, however, stand in the way of such a complete solution of the problem, and for the present we must content ourselves with showing that the observed values of the constants mentioned are not unreasonable. To that end we shall assume a simple form for the potential energy function and shall study the variation in the frequency of vibration with the angular velocity and with the vibrational energy on the basis of the restricting hypothesis that the amplitude of the vibrations is small.

All that we can reasonably feel sure of in regard to the law of force which governs the motion of the atoms is that it is asymmetric in that the potential energy increases more rapidly when the atoms are compressed together than when they are drawn apart. A simple formula having the asymmetry suggested is obtained if the force is assumed to be composed of a constant attraction combined with a repulsion varying inversely as the nth power of the distance between the nuclei. The net repulsive force between the atomic centers will then be given by an expression of the form

$$- \Phi'(\zeta) = \alpha\zeta^{-n} - \beta, \qquad (23)$$

where α and β are constants.

Since the force reduces to zero when ζ equals ζ_0,

$$\beta = \alpha/\zeta_0{}^n.$$

Equation (10) becomes

$$m\frac{d^2\zeta}{dt^2} = \alpha\left[\frac{1}{\zeta^n} - \frac{1}{\zeta_0{}^n}\right] + \frac{m\Omega_0{}^2\zeta_0{}^4}{\zeta^3}. \qquad (24)$$

In order to integrate (24) we will throw it into the form (4) by means of approximations. Consider first the case where the angular velocity is zero. In this case it is convenient to expand $1/\zeta^n$ and $1/\zeta^3$ into power series about the point $\zeta = \zeta_0$. Let

$$\xi = \zeta - \zeta_0.$$

Then (24) is readily transformed into

$$m\frac{d^2\xi}{dt^2} = -\frac{\alpha n}{\zeta_0{}^{n+1}}\cdot\xi + \frac{\alpha n(n+1)}{2\zeta_0{}^{n+2}}\cdot\xi^2 + \cdots. \qquad (25)$$

Neglecting the terms containing the cube and higher powers of ξ, we can throw (25) into the form (4) by establishing the relationships

$$k = \alpha n/\zeta_0{}^{n+1}; \qquad (26a)$$

$$k_2 = -\alpha n(n+1)/2\zeta_0{}^{n+2}. \qquad (26b)$$

According to Seeliger[1] the following equations constitute an approximate solution of (4):

$$\xi = A'\cos 2\pi\omega_0 t + A''\cdot\cos 4\pi\omega_0 t + \text{const.}, \qquad (27a)$$

$$A' = A\left(1 + \frac{Ak_2}{3k}\right), \qquad (27b)$$

$$A'' = A^2k_2/6k, \qquad (27c)$$

$$\omega_0' = \frac{1}{2\pi}\sqrt{k/m}, \qquad (27d)$$

$$\omega_0 = \omega_0'\left[1 - \frac{5}{12}A^2\left(\frac{k_2}{k}\right)^2\right]. \qquad (27e)$$

In case the angular velocity is not zero, the molecule expands under the influence of centrifugal force, so that the equilibrium value of ζ changes from ζ_0 to ζ_1, where ζ_1 is a root of the equation

$$\alpha\left(\frac{1}{\zeta^n} - \frac{1}{\zeta_0{}^n}\right) + \frac{m\Omega_0{}^2\zeta_0{}^4}{\zeta^3} = 0. \qquad (28)$$

It is convenient to introduce the quantity $\Delta\zeta$ defined by the equation

$$\Delta\zeta = \zeta_1 - \zeta_0.$$

Expanding the left-hand member of equation (28) in series, neglecting terms containing the squares and higher powers of $\Delta\zeta$, and solving for $\Delta\zeta$, we obtain the approximate value

$$\Delta\zeta = \frac{m\Omega_0{}^2\zeta_0}{\dfrac{\alpha n}{\zeta_0{}^{n+1}} + 3m\Omega_0{}^2}.$$

By the introduction of the frequency of rotation ν_r and by the use of equations (26a) and (27d) the above can be reduced to

$$\Delta\zeta = \frac{\zeta_0\nu_r{}^2}{\omega_0'^2 + 3\nu_r{}^2}.$$

Since the frequency of rotation ν_r is for all cases under consideration

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[1] R. Seeliger, Verh. d. D. Physik. Ges., 16, p. 1042, 1914.

quite small compared with the frequency of vibration, we can neglect $3\nu_r^2$ in comparison with $\omega_0'^2$. Hence

$$\Delta\zeta = \zeta_0\nu_r^2/\omega_0'^2. \tag{29}$$

Now let

$$\xi = \zeta - \zeta_1.$$

Expanding in series about the point ζ_1 and discarding higher order terms, we throw (24) into the form

$$m\frac{d^2\xi}{dt^2} = -\left[\frac{\alpha n}{\zeta_1^{n+1}} + \frac{3m\Omega_0^2\zeta_0^4}{\zeta_1^4}\right]\xi + \left[\frac{\alpha n(n+1)}{2\zeta_1^{n+2}} + \frac{6m\Omega_0^2\zeta_0^4}{\zeta_1'}\right]\xi^2. \tag{30}$$

Let k' and k_2' denote the values of k and k_2 when Ω_0 does not vanish.

$$\begin{aligned} k' &= \frac{\alpha n}{\zeta_1^{n+1}} + \frac{3m\Omega_0^2\zeta_0^4}{\zeta_1^4} \\ &= \frac{\alpha n}{\zeta_0^{n+1}} + 3m\Omega_0^2 - \Delta\zeta\left[\frac{\alpha n(n+1)}{\zeta_0^{n+2}} + \frac{12m\Omega_0^2}{\zeta_0}\right]. \\ -k_2' &= \frac{\alpha n(n+1)}{2\zeta_1^{n+2}} + \frac{6m\Omega_0^2\zeta_0^4}{\zeta_1^5} \\ &= \frac{\alpha n(n+1)}{2\zeta_0^{n+2}} + \frac{6m\Omega_0^2}{\zeta_0} - \frac{\Delta\zeta}{\zeta_0^2}\left[\frac{\alpha n(n+1)(n+2)}{2\zeta_0^{n+1}} + 30m\Omega_0^2\right]. \end{aligned}$$

By means of further approximations and with the help of equations (26*a*), (27*d*), and (29) the above expressions for k' and k_2' can be reduced to

$$k' = 4\pi^2 m\omega_0'^2\left[1 - (n-2)\frac{\nu_r^2}{\omega_0'^2}\right], \tag{31}$$

$$k_2' = -\frac{4\pi^2 m\omega_0'^2}{\zeta_0}\left[\frac{n+1}{2} - \left\{\frac{(n+1)(n+2)}{2} - 6\right\}\frac{\nu_r^2}{\omega_0'^2}\right]. \tag{32}$$

Hence

$$k_2'/k' = -\frac{n+1}{2\zeta_0}\left[1 - \left\{4 - \frac{12}{n+1}\right\}\frac{\nu_r^2}{\omega_0'^2}\right]. \tag{33}$$

Let ω denote the frequency of vibration corresponding to the angular frequency ν_r. Then

$$\begin{aligned} \omega &= \frac{1}{2\pi}\sqrt{\frac{k'}{m}}\left[1 - 5/12\,A^2\left(\frac{k_2'}{k'}\right)^2\right] \\ &= \omega_0'\left\{1 - \frac{5}{48}\left(\frac{A}{\zeta_0}\right)^2(n+1)^2\right. \\ &\qquad \left. - \left[\frac{n-2}{2} - \left(8 - \frac{24}{n+1}\right)\frac{5}{48}(n+1)^2\left(\frac{A}{\zeta_0}\right)^2\right]\frac{\nu_r^2}{\omega_0'^2}\right\}. \end{aligned} \tag{34}$$

Comparing equations (13) and (34) we see that

$$a = \frac{1}{\omega_0'}\left[\frac{n-2}{2} - \left(8 - \frac{24}{n+1}\right)\frac{5}{48}(n+1)^2\left(\frac{A}{\zeta_0}\right)^2\right]. \tag{35}$$

It is to be expected on the basis of the attempts which have been made to formulate a law governing the mutual repulsion of whole molecules that n will have a value between 5 and 15. That being the case, it will be observed that for small values of A (which is a measure of the amplitude of the vibration) a is a positive quantity whose value decreases with the energy of vibration. A qualitative agreement between the observed values of $\mathfrak{A}$ and $\mathfrak{A}'$ and the equations (20) and (21), or (22) is thus established.

The writer has shown elsewhere that in the case of HCl the ratio A/ζ_0 should be in the neighborhood of 0.12 when $\tau = 1$. The above approximate equations are certainly not valid for such large amplitudes of vibration as this, but it is of interest to apply them even out of the range in which they are properly applicable.

The square of A is roughly proportional to the energy of vibration, which, in turn, is roughly proportional to τ. Hence we may substitute $(0.12)^2\tau$ for A/ζ_0 in (35). The observed values of N and N' are 8.655×10^{-14} and $2 \times 8.49 \times 10^{-14}$ respectively, from which we may assume, on the basis of equations (22), that 8.8×10^{-14} is not far from the correct value of $\omega(0, 0)$, or ω_0'. Substituting these values into (35) and giving n the value 7.5, we obtain

$$a = (3.125 - 0.638\tau) \times 10^{-14}.$$

Equations (22), based on the assumption that the vibrational energy may be reduced to zero, then give $\mathfrak{A} = 2.5 \times 10^{-14}$ and $\mathfrak{A}' = 3.7 \times 10^{-14}$. The observed values of these constants are $\mathfrak{A} = 2.55 \times 10^{-14}$ and $\mathfrak{A}' = 3.7 \times 10^{-14}$ respectively, so that the agreement is excellent. On the other hand it is not possible to choose any value of n which will give good values of either $\mathfrak{A}$ or $\mathfrak{A}'$ if we assume that equations (20) and (21) are correct.

The internal evidence of our theory therefore favors the hypothesis that for vibrational motion zero is one of the possible values of τ. In other words, there is no "zero-point energy" for vibrational degrees of freedom such as that which the Bohr theory assumes for the rotational degrees of freedom. Too much weight should not be attached to this result, however, since the equations on which it is based are admittedly inaccurate and give excessively large differences between the frequencies N' and $2N$.

Kirchhoff's Law.

The problem of giving quantitative proof that the present extension of Bohr's theory is in harmony with Kirchhoff's law is substantially equivalent to the problem of deriving Planck's radiation formula from the theory in question, and it involves the introduction of hypotheses which are outside the scope of the present paper. The writer will therefore content himself here with a qualitative discussion of the relation of the theory to Kirchhoff's law in the hope that he may later have the privilege of taking up the problem in a quantitative manner.

Kirchhoff's law rests on the proposition that the ratio of the coefficient of emission of any medium for the frequency ν to its coefficient of absorption for the same frequency when in a state of thermodynamic equilibrium is equal to the specific intensity of black radiation for the same temperature and frequency divided by the square of the index of refraction.[1] If we assume (following in the footsteps of Planck) that we have to do with a gaseous medium of very low density, we may call the index of refraction unity. Denoting the coefficients of emission and absorption by ϵ_ν and α_ν respectively, and the intensity of black radiation by K_ν, we have

$$\frac{\epsilon_\nu}{\alpha_\nu} = K_\nu.$$

Let ν' denote any other frequency. Then

$$\frac{\epsilon_\nu'}{\alpha_\nu'} = K_\nu',$$

and by Planck's radiation law

$$\frac{\epsilon_\nu}{\epsilon_{\nu'}} \div \frac{\alpha_\nu}{\alpha_\nu} = \left(\frac{\nu}{\nu'}\right)^3 \left[\frac{e^{h\nu'/kT} - 1}{e^{h\nu/kT} - 1}\right]. \tag{36}$$

Equation (36) must be satisfied for any two frequencies ν and ν', if Kirchhoff's law is to be satisfied, and conversely we may apply (36) to the theory of harmonics as a test of its compatibility with Kirchhoff's law.

In making this test, we may, to begin with, neglect the broadening of the absorption and emission bands by molecular rotations and by the Doppler effect. ϵ_ν and ϵ_ν' may then be replaced by the integrated intensities of the fundamental and harmonic emission bands, while α_ν and α_ν' are replaced by the corresponding intensities of the absorption bands. It should be observed that if we replace ν' by 2ν the right-hand member of (36) decreases from infinity for very small values of the temperature T to one fourth for very large values of T. Consequently

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[1] Cf. Planck's "Heat Radiation" (trans. by Masius), p. 35.

either the ratio of the emission coefficients $\epsilon_\nu \epsilon_{\nu'}$ must decrease greatly with increasing temperature or the ratio of the absorption coefficients $\alpha_\nu \alpha_{\nu'}$ must increase to the same extent.

Now according to the writer's earlier theory of harmonics the ratio of the intensities of the fundamental and harmonic bands was independent of the temperature for both the absorption and emission processes, in complete disaccord with (36). The present theory, on the other hand, provides for a large temperature variation in the relative emission from the two bands, although the ratio of the absorption percentages should be independent of the temperature. This is because the fundamental and harmonic emission bands have their origin in *different* groups of molecules, the relative numbers in which vary with the temperature. Thus, at the lowest temperatures the number of molecules in the second steady state is infinite compared with the number in the third, while at extremely high temperatures the numbers approach equality and the *relative* intensity of the fundamental emission band decreases correspondingly.

The above fact establishes a qualitative agreement between our new theory of harmonics and Kirchhoff's law and shows that the new theory meets all the difficulties encountered by the old in a qualitative manner, at least. It should be observed, however, that there is a minor contradiction to Kirchhoff's law involved in the Bjerrum theory of the structure of the infra-red absorption and emission bands upon which the present work is in part based. For if we let ν and ν' in equation (36) denote the frequencies of the two quantum lines in one of these bands which are due to the group of molecules having any one of the possible angular velocities, we get into the same trouble as in the writer's first theory of harmonics. The two elementary absorption bands are due to the same group of molecules and the two emission bands are due to the same group. Consequently the ratio of the intensities of the absorption bands and the ratio of the intensities of the two emission bands should apparently each be independent of the temperature. As the Bjerrum theory is very well established the above consideration seems to force the conclusion that, while equation (36) may be, and probably is, correct when applied to regions of the spectrum which are far apart, it cannot hold when applied to narrow strips of the spectrum which are very close together. In other words, Kirchhoff's law and the rule that the ratio of the intensity of radiation inside any body or substance in thermodynamic equilibrium to the square of the index of refraction is a universal function of the temperature and frequency, while approximately correct as broad generalizations, are not strictly true when applied to the comparison of closely adjacent portions of the spectrum.

Supplementary Note.

Since placing the above paper in the hands of the publishers, my attention has been called to the formulation of the quantum condition for the determination of the steady states of motion by W. Wilson (Phil. Mag., 29, pp. 795–802, June, 1915), and the arrival of the long delayed copies of the Annalen der Physik for 1916 has put into my hands the independent formulation of this same hypothesis by Sommerfeld, together with his brilliant explanation of the complex structure of the lines in the spectra of hydrogen and ionized helium by its aid.

The quantum condition in question takes the form of the requirement that certain of the generalized coördinates of the atomic or molecular systems in question shall satisfy equations of the form

$$\int p\,dq = \tau h,$$

where p is the momentum corresponding to the coördinates q, h is Planck's constant, τ is an integer, and the integration is to be extended over a complete cycle of values of q. Applying this condition to the vibration of a diatomic molecule we obtain

$$\int m\dot{\zeta}\,d\zeta = 2\int T\,dt = \tau h,$$

or

$$\overline{T} = \frac{\tau}{2} h\omega.$$

Here, as in the text above, T and ω denote the kinetic energy and the vibrational frequency respectively.

If we assume, as a first approximation, that the mean values of the kinetic and potential energies are sensibly equal, we obtain equation (1) above.

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