ON THE OCCURRENCE OF HARMONICS IN THE INFRA-RED ABSORPTION SPECTRA OF GASES.

By Edwin C. Kemble.

Introduction.

In the preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules" we have given a brief account of Bjerrum's theory of the structure of the infra-red absorption bands of gases and of the direct and conclusive evidence which that theory has given in favor of that older form of the quantum theory according to which the vibrating atoms and electrons can have only energies which are integral multiples of $h\nu$ (the rotational energies, on the other hand, being multiples of $h\nu/2$). The application of this theory to the vibrations of the atoms in a diatomic gas molecule shows that the minimum amplitude of these oscillations must be an appreciable fraction of the mean distance between the atomic centers. In the present paper we propose to show that owing to the large amplitude of these oscillations and the nonlinearity of the law of force between the atoms it is to be expected that the strong infra-red absorption bands to which these vibrations give rise should be accompanied by faint harmonics. Such an harmonic does occur in the infra-red spectrum of carbon monoxide and we will give a number of reasons for believing that its occurrence is not accidental. Another result of the application of this form of the quantum theory to these atomic vibrations is the prediction of new infra-red absorption bands at high temperatures. In conclusion we will give some new evidence from the width of these bands in favor of the hypothesis that the vibratory energy must be a multiple of $h\nu$.

Reason for the Occurrence of Faint Harmonics.

Consider the vibratory motion of the atoms in a diatomic gas molecule. The restoring force will not be strictly proportional to the relative displacement from the position of equilibrium. Consequently, while the motion will be periodic no matter what the amplitude,[1] it will be approximately simple harmonic only for very small amplitudes. The accelera-

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[1] This would not be true if the motion were damped by radiation, but of course there can be no such damping if the process of radiation is discontinuous.

tion corresponding to such a periodic non-sinusoidal motion of frequency ν, if it be expressed by means of circular functions at all must be expressed as a Fourier's series in sines and cosines of integral multiples of $2\pi\nu t$.

Turn for a moment to the radiation and absorption in the extreme infra-red due to the rotation of the polarized molecules. According to the classical mechanics and electrodynamics we should expect that as a rotating molecule absorbs energy its frequency of rotation should increase and with that the frequency of the radiation absorbed. Whether the radiation be absorbed by quanta or not we should expect that the molecule would absorb light of all frequencies between that of its rotation before absorption and that of its rotation after absorption. But as a matter of fact the absorption seems to be all from a small frequency interval in the immediate neighborhood of the final frequency of rotation. This fact seems to make plausible the general assumption that *the character of the radiation emitted or absorbed by an oscillator is determined by the character of the motion of the atoms before emission begins or after absorption has taken place.*

It follows at once from this assumption that *the radiation or absorption from a non-sinusoidal periodic oscillation should consist of an infinite series of lines of gradually decreasing intensity whose frequencies are integral multiples of the frequency of the fundamental* (each term in the above-mentioned Fourier's series giving rise to a line). Of course we should hardly expect that more than two or three of the harmonics would have sufficient intensity to be detected experimentally.

Another consequence of the lack of linearity in the relation between the restoring force and the displacement is that the frequency of vibration depends on the amplitude. This point will be taken up again later on.

It is not difficult to show that the departure of the motion from the simple harmonic type must be considerable. Consider the vibratory motion of the atoms in a diatomic molecule having one quantum of energy. It will be assumed that the motion takes place in accordance with the classical mechanics. Let m_1 and m_2 be the masses of the two atoms and let r denote the distance between the nuclei. Let $F(r)$ denote the force exerted by each atom on the other, a repulsion being taken as positive. Then it may very easily be shown that the equation of motion is

$$m\frac{d^2r}{dt^2} = F(r), \tag{1}$$

where

$$m = \frac{m_1 m_2}{m_1 + m_2}. \tag{1a}$$

Let r_0 denote the value of r for which the force vanishes, *i. e.*, the distance between the nuclei when the two atoms are in equilibrium and write

$$x = r - r_0.$$

Expanding $F(r)$ in a Taylor's series we may throw (1) into the form

$$m\frac{d^2x}{dt^2} = x\left(\frac{dF}{dr}\right)_{r=r_0} + \frac{x^2}{2!}\left(\frac{d^2F}{dr^2}\right)_{r=r_0} + \frac{x^3}{3!}\left(\frac{d^3F}{dr^3}\right)_{r=r_0} + \cdots. \tag{2}$$

For sufficiently small values of x the terms after the first will always be negligible and the force will be a linear function of the displacement. But if the displacements are not small the terms of higher order than the first must be taken into account. However, we may obtain an approximate idea of the amplitude of the oscillation if we neglect these higher order terms. Let A denote this unknown amplitude. Then the approximate value of the energy will be $2\pi^2 m\nu^2 A^2$. Equating the energy to $h\nu$ we obtain

$$A = \frac{1}{\pi}\sqrt{\frac{n}{2m\nu}}. \tag{3}$$

HCl is a typical diatomic gas. It has a single infra-red absorption band, a doublet with maxima at 3.40 μ and 3.55 μ respectively. The corresponding fundamental frequency is 8.64×10^{13} vibrations per second. Substituting the masses of the hydrogen and chlorine atoms for m_1 and m_2 respectively we obtain

$$m = \frac{35.5 \times 1.64 \times 10^{-24}}{35.5 + 1.0} = 1.60 \times 10^{-24} \text{ gm.}$$

If 6.4×10^{-27} be taken as the value of h, the amplitude computed from (3) is 1.53×10^{-9} cm., or about 12 per cent. of the normal distance between the nuclei.[1]

We are of course ignorant of the exact form of the law of force, but it is obvious that it cannot be even approximately linear for such large relative displacements as that just computed. The common assumption regarding the law of intermolecular repulsion is that it is of the form

$$f(r) = Ar^{-n}, \tag{4}$$

where n is a positive number. The values suggested for n vary from five

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[1] The moment of inertia of the HCl molecule is 2.7×10^{-40} gm. cm.^{2} (cf. preceding paper on "The Distribution of Angular Velocities Among Diatomic Gas Molecules"). Assuming that the masses m_1 and m_2 of the two atoms are concentrated in the nuclei whose distance apart is r_0 we obtain the expression

$$J = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

for the moment of inertia. Substituting into this formula the numerical values of J, m_1 and m_2 and solving for r_0 we obtain $r_0 = 1.30 \times 10^{-8}$ cm.

to fifteen. It seems plausible to assume for the law of interatomic force the analogous form

$$F(r) = ar^{-n} - b.^{1} \qquad (5)$$

Giving n the small value 5 and expanding in series we obtain

$$F(r_0 + \Delta r) = - 5ar_0^{-6}\Delta r + 30ar_0^{-7}\frac{(\Delta r)^2}{2!} - 210ar_0^{-8}\frac{(\Delta r)^3}{3!} + \cdots.$$

Put

$$\Delta r = - 0.12r_0.$$

Then the ratio of the second degree term to the first degree term takes the value 0.36 and the ratio of the third degree term to the first degree term becomes 0.11. The ratio of the sum of the first three nonlinear terms to the linear terms is 0.48. In other words, if the law of force were as assumed, the force acting between the atoms at this extremity of the vibration would be half again as great as that computed on the assumption that the force is a linear function of the displacement. For larger values of n the effect of the nonlinear terms would be even greater.

This preliminary computation is for a molecule having a single quantum of vibratory energy. But the ratio of the number of molecules which have one quantum of vibratory energy at the temperature T to the number which have no vibratory energy is $e^{h\nu/kT}$. The numerical value of this ratio for HCl at 18° C. is 1.5×10^6. This is also the ratio of the number which have one quantum to the number which have two. Consequently practically all the absorption must be due to the molecules which are taking up their first quantum of vibratory energy and the character of the radiation absorbed must be determined by the character of the vibration corresponding to one quantum of energy.

EXPERIMENTAL CONFIRMATION.

Perhaps the most careful investigation of the infra-red absorption spectra of the simpler gases made thus far was that of Burmeister.[2] He examined four diatomic gases, Cl_2, HCl, Br_2 and HBr, between the wave-lengths 1 μ and 18 μ with great care. Investigation of the absorption in certain regions of the infra-red spectra of three other diatomic gases, H_2, O_2 and CO, was also made and these observations together with those of other investigators give exact information regarding the infra-red absorption spectra of these gases over the region in which the first four were examined. Considerable pains were taken to eliminate impurities.

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[1] The attractive force b is probably not constant but its rate of variation must be small compared with that of the repulsive force.

[2] W. Burmeister, Verh. d. D. Phys. Ges., 15, p. 589, 1913.

None of the gaseous elements, H_2, O_2, Cl_2, Br_2, has any infra-red absorption bands. In view of Drude's theory of the origin of these bands[1] this is not surprising, for it is not to be expected that the atoms in these otherwise symmetrical molecules should turn out to bear charges of opposite sign. In fact the absence of infra-red absorption bands in the spectra of these elementary gases is a confirmation of the view that the bands in this region are due wholly to atomic vibrations, for it shows that these bands are peculiar to those gases whose atoms are charged. HCl and HBr have each but one double absorption band. CO has a strong double band with maxima at 4.60 μ and 4.72 μ and a weak band with a single observed maximum at 2.35 μ.[2]

The writer is of the opinion that the occurrence of a weak band in the absorption spectrum of carbon monoxide at nearly half the mean wave-length of the strong dobule band near 4.60 μ is not accidental, but is a true example of the kind of harmonics predicted by our theory.

As evidence in favor of this view we observe in the first place that the band meets the three *necessary* conditions imposed by the theory. (*a*) The wave-length is right. A careful remeasurement of Burmeister's absorption curve indicates that the maximum of the faint band is nearer 2.34 μ than 2.35 μ. The wave-length corresponding to the mid-point between the maxima of the double band is 4.66 μ. Thus the discrepancy between the half wave-length of the strong band and the wave-length of the weak band is only 0.01 μ, an amount easily within the limit of experimental error. (*b*) The relative intensity of the two bands is right, *i. e.*, the fundamental is much more intense than the harmonic. (*c*) The character of the harmonic agrees with that of the fundamental. Both bands are fairly symmetrical and their relative widths check fairly well with the theory. The formula for the separation of the two components into which any line is split by the molecular rotation[3] shows that this separation should be proportional to the square of the average wave-length. Consequently the width of the harmonic should be one fourth of the width of the fundamental. Measurement of Burmeister's curves shows that the band at 2.34 μ is actually about one third the width of that at 4.66 μ. The correction to be made to pass from total absorption to absorption coefficient increases the discrepancy, but on account

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[1] Cf. introduction to the preceding paper on "The Distribution of Angular Velocities, etc."

[2] Cf. Fig. 2 of the preceding paper.

[3] The formula is

$$\lambda_1 - \lambda_2 = 2\frac{\lambda_1\lambda_2}{\lambda_r},$$

where λ_1 and λ_2 are the wave-lengths of the two components and λ_r is the wave-length corresponding to the most probable frequency of rotation. (Cf. preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules.")

of the low dispersion, which was quite insufficient to separate the components of the harmonic, the determination of its width is so uncertain that the agreement between theory and experiment on this point need not be considered unsatisfactory.

A second reason for believing that the band at 2.34 μ is a true harmonic of the one at 4.66 μ is the difficulty in accounting for the former in any other way. A diatomic molecule can have but one atomic vibration. Therefore, if the band at 2.34 μ is not a bonafide harmonic of the band at 4.66 μ, it must be due either to an impurity or to an electronic vibration inside the atom. The care with which Burmeister tested these bands seems to rule out the first alternative. There are two reasons for supposing that this band is not due to an electronic vibration. In the first place, absorption bands not due to atomic vibrations in the infra-red spectra of diatomic gases between, say, 1.5 μ and 15 μ are rare, if they occur at all. In none of the seven diatomic gases examined by Burmeister with the exception of CO is there more than the one band due to the atomic vibration. More generally, it is possible to predict from the number of atoms in the more complicated molecules the number of normal modes of vibration which the atoms should have and in none of the absorption spectra of the four gases examined by Burmeister having three or more atoms per molecule are there more bands than there are modes for the corresponding molecules. Coblentz[1] found exceptions to this rule in the gases H_2S, SO_2 and NH_3 but the extra lines which he noted may be due to impurities against which he could not guard so completely in his very extensive survey of absorption spectra or (as some of the lines are faint) they may be due to the nonlinearity of the law of force.[2] The other reason for supposing that the band at 2.34 μ in the spectrum of CO is not due to an electronic vibration is that like the other infra-red absorption bands under discussion it has a different character from that usual among the bands in the visible.[3] The latter generally have a strong head from which they gradually fade away on one side or have a wavy fluctuation in intensity.

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[1] W. W. Coblentz, Investigations of Infra-red Spectra, Washington, 1905.

[2] It does not follow from the fact that the failure of Hook's law for large vibrations in a diatomic molecule introduces new absorption and emission bands which are harmonics of the fundamental that the same rule holds for molecules having three or more atoms. In the case of the diatomic molecules the motion is necessarily strictly periodic for any amplitude and for this reason the acceleration may be analyzed into a Fourier's series of sine functions of integral multiples of $2\pi\nu t$. But apparently the motion of more complicated atomic systems need not follow this rule and it may be that the effect of the failure of Hook's law is in this case to introduce faint absorption bands which are not harmonics of the fundamental bands corresponding to the normal modes of oscillation for infinitesimal energies.

[3] See, for instance, Konen, Das Leuchten der Gase und Dämpfe, Braunschweig, 1913, p. 245.

The writer has also examined the charts given by Coblentz in his "Investigations of Infra-red Spectra" for other cases of harmonic absorption bands. Coblentz himself, after remarking that a search for harmonic absorption bands is generally considered illusory, calls attention to their frequent occurrence in the infra-red spectra of the organic substances examined by him. For instance, a great many hydrocarbons show a very strong band at 3.4 μ and a weak one at about 1.7 μ. Thiophene shows a strong band at 9.29 μ and a weak one at 4.60 μ. Acetylene shows similar bands at 7.4 μ and 3.7 μ; butane at 8.90 μ and 4.45 μ; ethylene at 10.5 μ and 5.27 μ; carvacrol at 12.3 μ and 6.13 μ with another pair of bands at 10.09 μ and 5.04 μ and still another at 8.08 μ and 4.01 μ; ethyl iodide at 10.5 μ and 5.28 μ; methyl acetate at 9.6 μ and 4.78 μ; selenite at 2.97 μ and 1.44 μ. Water shows a weak band at 1.50 μ, a strong one at 2.97 μ and one of medium intensity at 5.99 μ. The harmonic ratio between the last two bands must be regarded as accidental since the band corresponding to the greater wave-length is the less intense. It is difficult to say to what extent the occurrence of these bands having wave-lengths in harmonic ratios is accidental and to what extent they are the result of non-sinusoidal periodic vibrations. The bands are apt to be broad and the determination of wave-lengths is uncertain. A careful remeasurement of the positions of the maxima of the bands in question would be instructive. We have already remarked (footnote, p. 706) that the bands introduced into the absorption spectra of gases having more than two atoms to the molecule need not be exact harmonics of the fundamental frequencies. On the other hand it seems probable from analogy with the diatomic case that they would frequently be nearly so.

The Dependence of Frequency on the Amplitude.

In addition to destroying the simple harmonic character of the motion the lack of linearity in the relation between displacement and restoring force in the case of diatomic molecules will make the frequency a function of the amplitude of the motion. R. Seeliger[1] has recently given a discussion of the effect of terms of the second degree in the displacement on the motion of an oscillator and the energy which it emits, in which he deduces a relation between the breadth of an emission line, the magnitude of the second degree term and the rate at which energy is radiated, on the assumption that the emission of energy is in accordance with the classical electrodynamics and that the vibrators have all amplitudes between zero and a certain maximum. On this theory the width and

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

position of an absorption line should depend on the temperature of the absorbing medium. But on the basis of the older form of the quantum theory for which we claim decisive evidence practically all the energy will be absorbed by molecules which originally had no vibratory energy and which after absorption have a single quantum. These molecules have a single definite frequency independent of the temperature. If the molecule can absorb two quanta of energy without splitting apart a second absorption band at a different position should begin to appear at very high temperatures. At 1,000° C. about 9 per cent. of the molecules would have one quantum and 0.8 per cent. would have two. Consequently the absorption band due to the molecules having two quanta would have an intensity of the order of magnitude of one tenth of the intensity of the band at 4.6 μ at this temperature.

POSITION OF HIGH TEMPERATURE BAND OF CARBON MONOXIDE.

A rough idea of the position of this high temperature band may be obtained from the relative intensities of the bands at 4.6 μ and 2.3 μ. An approximate solution of the equation of motion (2) may be obtained by neglecting all but the first two terms of the right-hand member. The equation then takes the form

$$m\frac{d^2z}{dt^2} = -kz - k_2z^2. \tag{6}$$

Seeliger (l. c.) gives the following approximate solution of (6).

$$z = A' \cos 2\pi\nu t + A'' \cos 4\pi\nu t + \text{Const.}, \tag{7}$$

where

$$A' = A\left(1 + \frac{Ak_2}{3k_2}\right), \tag{8}$$

$$A'' = \frac{A^2k_2}{6k}, \tag{9}$$

$$\nu = \nu_0\left[1 - \tfrac{5}{12}A^2\left(\frac{K_2}{K}\right)^2\right], \tag{10}$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}. \tag{11}$$

We assume that the waves radiated have the same form that they would have according to the classical electrodynamics if the motion of the vibrating atoms were not damped by the radiation. Let E' and E'' be the energies radiated of frequencies ν and 2ν respectively. Then

$$\frac{E'}{E''} = \frac{A'^2\nu^2}{A''^2 4\nu^2}$$

or

$$\frac{A'}{2A''} = \pm\sqrt{\frac{E'}{E''}}. \tag{12}$$

Granting that the ratio, E'/E'', of the intensities of the two emission bands can be determined from the relative intensities of the corresponding absorption bands, it is possible to compute all the constants characteristic of the motion. From (8), (9) and (12) we have

$$A' = A + 2A'' = A - A'\sqrt{\frac{E''}{E'}},$$

or,

$$A = A'\left(1 + \sqrt{\frac{E''}{E'}}\right), \tag{13}$$

if we choose the positive sign in (12). The energy is all kinetic when d^2z/dt^2 vanishes, *i. e.*, when

$$A' \cos 2\pi\nu t + 4A'' \cos 4\pi\nu t = 0.$$

Substitute the symbol x for $2\pi\nu t$ and solve the above equation for $\cos x$. Thus

$$\cos x = \frac{1}{8}\left[-\frac{A'}{2A''} \pm \sqrt{\frac{A'^2}{4A''^2} + 32}\right]$$

or

$$x = \cos^{-1}\left[\frac{1}{8}\sqrt{\frac{E'}{E''}} \pm \frac{1}{8}\sqrt{\frac{E'}{E''} + 32}\right]. \tag{14}$$

Denote the set of roots of this equation corresponding to the numerically smaller value of $\cos x$ by x_1. The total energy of the molecule is then equal to its kinetic energy when $x = x_1$, *i. e.*,

$$\begin{aligned} e = \tfrac{1}{2}m\left(\frac{dz}{dt}\right)^2_{x=x_1} &= 2m\pi^2\nu^2(A' \sin x_1 + 2A'' \sin 2x_1)^2 \\ &= 2m\pi^2\nu^2A'^2\left(\sin x_1 - \sqrt{\frac{E''}{E'}} \sin 2x_1\right)^2. \end{aligned} \tag{15}$$

We do not know what the size of a quantum is for a non-sinusoidal periodic motion but we may be reasonably sure that it must have $h\nu$ as a limit when the motion approaches the simple harmonic type. Hence $h\nu$ may be taken as an approximate value of the energy. Substituting $h\nu$ for e in (15) the equation may be solved for A' in terms of known quantities.

$$A' = \sqrt{\frac{h}{2m\nu}}\,\frac{1}{\pi(\sin x_1 - \sqrt{E''/E'} \sin 2x_1)}. \tag{16}$$

Having obtained the numerical value of A', the equations (12), (13), (9), (10) and (11) enable us to compute the values of k_2/k, ν_0, k and k_2 in turn.

But in order to get any of these quantities we must first obtain the value of E'/E'' from the absorption curves. The question of the relation between emission and absorption is a very difficult one. Kirchhoff's law certainly cannot hold here, for it says that the ratio of the energy emitted by a body at the temperature T in the frequency interval $d\nu$ to the coefficient of absorption for that interval is proportional to the intensity of black radiation of frequency ν. But at room temperature the intensity of black radiation at 4.6 μ is enormously greater than the corresponding intensity at 2.3 μ.[1] Consequently the ratio of the intensities of the absorption bands at 2.3 μ and at 4.6 μ would be enormously greater than the ratio of the emission bands, and the slightest departure from linearity in the law of force would produce a very strong absorption band at 2.3 μ. Such an assumption is entirely inadmissible.

In the absence of any detailed knowledge of the nature of the process of absorption we are forced to make the most plausible assumption possible regarding the ratio of the intensities of the two bands. According to the classical electrodynamics[2] the rate at which an ideal linear oscillator of frequency ν, in which the restoring force is strictly proportional to the displacement, absorbs energy is proportional to K_ν/β where K_ν is the intensity of the radiation per unit frequency which flows past it and β is the mass coefficient. Let ν' denote the fundamental frequency of the vibrations of any diatomic molecule and let ν'' denote the frequency of the first harmonic. For the present the effect of the molecular rotations will be neglected. We assume that when a beam of light of intensity K_ν and solid angle $d\Omega$ is passed through the gas each molecule will in a unit of time on the average absorb the energy $\gamma' K_{\nu'} d\Omega$ from the frequencies in the immediate neighborhood of ν' and the energy $\gamma'' K_{\nu''} d\Omega$ from the frequencies in the neighborhood of ν''. We further assume that the ratio of the molecular absorption coefficients per molecule, γ' and γ'', is equal to the ratio of the energies emitted in the corresponding emission bands, *i. e.*, that

$$\frac{\gamma'}{\gamma''} = \frac{E'}{E''}. \tag{17}$$

Let ν_r be the frequency of rotation of any given molecule. The effect of this rotation on the emission is to split the energy which would other-

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[1] Let ν' and ν'' denote the frequencies corresponding to the centers of the bands at 4.6 μ and 2.3 μ respectively. Then the ratio of the corresponding intensities at 290° absolute is

$$\frac{K_{\nu'}}{K_{\nu''}} = \frac{\nu'^3}{\nu''^3} \frac{e^{\frac{h\nu''}{KT}} - 1}{e^{\frac{h\nu'}{KT}} - 1} = \frac{1}{8} \frac{e^{\frac{6,290}{290}} - 1}{e^{\frac{3,120}{290}} - 1} = 5,800.$$

[2] Cf. J. H. Jeans, Report on Radiation and the Quantum-Theory, London, 1914, pp. 12–13.

wise be radiated at the frequency ν' into two parts having the frequencies $\nu' + \nu_r$ and $\nu' - \nu_r$.[1] Similarly, radiation which would otherwise be sent out with the frequency ν'' is split up into parts having the frequencies $\nu'' + \nu_r$ and $\nu'' - \nu_r$. We will call the first pair of frequencies the effective frequencies of the fundamental and the second pair the effective frequencies of the first harmonic. The effect of the rotation on the absorption is to split the absorption lines due to the group of molecules having any given frequency of rotation into two lines having each the corresponding effective frequency. The energy absorbed by a thin layer of gas from the frequency interval $d\nu$ of a beam of intensity K_ν and solid angle $d\Omega$ is proportional to $\gamma' K_\nu d\Omega(dN/d\nu)d\nu(= \gamma' K_\nu d\Omega(dN/d\nu_r)d\nu_r)$, where $(dN/d\nu)d\nu$ is the number of molecules per unit volume having their fundamental effective frequencies in the interval $d\nu$, if that interval is close to the fundamental frequency ν_0'. If $d\nu$ is near ν_0'' the energy absorbed is proportional to $\gamma'' K_\nu d\Omega(dN/d\nu)d\nu(= \gamma'' K_\nu d\Omega(dN/d\nu_r)d\nu_r)$. The corresponding absorption coefficients are

$$\alpha' = a\gamma' \frac{dN}{d\nu_r},$$

$$\alpha'' = a\gamma'' \frac{dN}{d\nu_r},$$

α', α'' and $dN/d\nu_r$ are functions of ν_r, but for any given value of ν_r, $dN/d\nu_r$ will have the same value in the expression for α' as in that for α''. Therefore

$$\frac{\alpha'}{\alpha''} = \frac{\gamma'}{\gamma''} = \frac{E'}{E''} \tag{18}$$

if α' and α'' are measured at corresponding points of the two absorption bands.

The task of evaluating E'/E'' is then equivalent to that of finding the ratio of the absorption coefficients at corresponding points of the two curves as given by Burmeister. Owing presumably to the fact that the slit widths employed in investigating the two curves for CO did not cover equal frequency intervals, the high frequency band is somewhat more flattened than the other (cf. p. 705) and for this reason the writer has plotted the absorption coefficients as ordinates against rotation frequencies as abscissas and taken the ratio of the areas under the two curves as the measure of E'/E''. The method of computing the values of the absorption coefficients from the values of the total absorption in a finite length of tube as given by Burmeister is described in the preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules."

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[1] Cf. introduction to preceding paper.

The computed value of E'/E'' for the two bands of carbon monoxide is 75. Hence

$$x_1 = 102^\circ\ 10'.$$

The value of m computed from (1a) is

$$m = 11.25 \times 10^{-24}\ \text{gm}.$$

Hence

$$\begin{aligned} A' &= 6.53 \times 10^{-10}\ \text{cm.},\\ A'' &= -\ 0.376 \times 10^{-10}\ \text{cm.},\\ A &= 7.28 \times 10^{-10}\ \text{cm.},\\ \nu &= c/\lambda = 6.44 \times 10^{13}\ \text{sec.}^{-1}\\ \nu_0 &= \nu/0.96 = 6.71 \times 10^{13}\ \text{sec.}^{-1} \end{aligned}$$

The energy will evidently be roughly proportional to A^2. Let ν' be the frequency of the molecules which have two quanta of energy. Its value may be obtained from (10) by substituting $2A^2$ for A^2. Thus

$$\nu' = \nu_0\left[1 - \frac{10}{12}\left(\frac{Ak_2}{K}\right)^2\right] = 6.17 \times 10^{13}.$$

The corresponding wave-length is

$$\lambda' = 4.87\ \mu.$$

The reader will observe by reference to Fig. 2 of the preceding paper that the maximum of the high temperature band comes close to the edge of the band due to the molecules which are taking up their first quantum of vibratory energy. Consequently the appearance of the former ought to be easily observable.

THE LAW OF INTERATOMIC FORCE.

It is of interest to compute the value of n in the law of force from the values of k and k_2 on the assumption that the law has the form (5). Expanding (5) in a power series in Δr we obtain

$$F(r_0 + \Delta r) = -\ nar_0^{-(n+1)}n\left[\Delta r - \frac{(n+1)(\Delta r)^2}{2r_0} + \cdots\right]. \tag{19}$$

Comparing with (6) we see that

$$\frac{k_2}{k} = -\frac{(n+1)}{2r_0}. \tag{20}$$

The value of r_0 computed from the separation of the maxima of the doublet at 4.66 μ is 1.10×10^{-8} cm. Also

$$\frac{k_2}{k} = \frac{6A''}{A_2} = -\ 0.428 \times 10^9.$$

Hence

$$n = -2r_2\frac{k^2}{k} - 1 = 8.43.$$

This result is in accord with the values of n elsewhere obtained for the law of intermolecular force.

Harmonics in the Absorption Spectra of Hydrochloric Acid and Hydrobromic Acid.

The absence of observable harmonics in the infra-red absorption spectra of HCl and HBr is difficult to explain. Owing to the small mass of the hydrogen atom the amplitude of the vibration should be much greater for these molecules and consequently the first harmonic should be relatively stronger than in the case of carbon monoxide. In fact, assuming that n has the value 8, the writer computes that the first harmonic in the spectrum of HCl should have an absolute intensity about three times as great as that of the first harmonic in the spectrum of CO. It is highly desirable that a careful search be made for these harmonics in the infra-red absorption spectra of HCl and HBr.

New Evidence for the Older Form of the Quantum Theory.

A consideration of the change in frequency with the amplitude gives new evidence in favor of the older form of the quantum theory which has been assumed throughout the present paper. This evidence is entirely independent of the theory advanced as to the nature of the carbon monoxide absorption band at 2.34 μ.

Assume that the law of force between the atoms of the carbon monoxide molecule is of the form (5) and give n the minimum value 5. Then k_2/k takes the value -2.73×10^8. For a molecule having one quantum of energy, A becomes 0.726×10^{-9} cm. and ν/ν_0 becomes 0.984. Hence

$$\nu - \nu_0 = 0.0164\nu_0.$$

The corresponding wave-length interval is 0.078 μ or about two thirds of the distance between the maxima of the double absorption band. (See Fig. 2 of the preceding paper.)

Now according to the later form of Planck's theory the absorbing molecules having any given rotational energy should have all vibrational energies between zero and one quantum. In fact they are assumed to be uniformly distributed over the "region element" between these extreme values of the energy. Consequently the molecules having any given rotational energy should absorb all wave-lengths between λ_0 and λ. They would give rise to a flat-topped elementary absorption band having a width two thirds as great as the distance between the maxima of the doublet. Under such conditions these maxima could not possibly be as sharply defined as they are.

Making the same computation for the HCl molecule, the width of the elementary absorption band due to the molecules having a single angular velocity turns out to be nearly *twice* the distance between the maxima of the observed absorption band. It is only possible to conclude that the process of absorption is in some way discontinuous so that the frequency of the absorbed radiation depends only on the final energy of the absorbing oscillator.

SUMMARY.

1. The writer has attempted to show that owing to the lack of linearity in the law of force between the atoms in a diatomic molecule the infra-red absorption band due to the vibration of the atoms along their line of centers should be accompanied by a faint harmonic.

2. The absorption bands at 2.34 μ and 4.66 μ in the spectrum of carbon monoxide have been adduced as an example of such harmonics and reasons have been given for believing that the relation between their wave-lengths is not accidental.

3. It has been shown that on the basis of the same theory it is to be expected that at sufficiently high temperatures a new band should appear near the fundamental low temperature band.

4. The position of this high temperature band for CO has been roughly computed.

5. From the magnitude of the faint harmonic in the carbon monoxide spectrum it has been computed that the force between the atoms must vary inversely as the 8.5th power of the distance between their nuclei.

6. It has been shown that the sharpness of the maxima of double absorption bands in the spectra of carbon monoxide and hydrochloric acid is incompatible with the newer form of the quantum theory in which absorption is supposed to take place gradually and not by quanta.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
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