SEPTEMBER 1, 1933 PHYSICAL REVIEW VOLUME 44

Intensity Distribution in a Band System of Symmetrical Triatomic Molecules

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(Received May 22, 1933)

The Franck-Condon theory has been extended to a study of band intensities of a triatomic molecule of the general type XY_2. The most probable transitions are found to be

$$v_1'=\begin{cases} A_1\pm B_1v_1^{\frac{1}{2}}\pm C_1v_2^{\frac{1}{2}}+D_1v_1+E_1v_2-F_1v_1-G_1v_2+H_1(v_1v_2)^{\frac{1}{2}} \\ A_1\pm B_1v_1^{\frac{1}{2}}\mp C_1v_2^{\frac{1}{2}}+D_1v_1+E_1v_2-F_1v_1-G_1v_2-H_1(v_1v_2)^{\frac{1}{2}} \end{cases}$$

$$v_2'=\begin{cases} A_2\pm B_2v_1^{\frac{1}{2}}\pm C_2v_2^{\frac{1}{2}}+D_2v_1+E_2v_2-F_2v_1-G_2v_2+H_2(v_1v_2)^{\frac{1}{2}} \\ A_2\pm B_2v_1^{\frac{1}{2}}\mp C_2v_2^{\frac{1}{2}}+D_2v_1+E_2v_2-F_2v_1-G_2v_2-H_2(v_1v_2)^{\frac{1}{2}} \end{cases}$$

$$v_3'=\begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3 \end{cases}$$

where the v's with and without a prime refer to the vibrational quantum numbers of the upper and lower states, respectively, and the values of the coefficients depend on the atomic masses, normal frequencies, force constants, and molecular dimensions. Two special cases which occur when the three atoms become equal and when the three atoms lie along a straight line are also considered. A wave mechanical treatment is outlined. It is found that for a triangular model the integrals, which measure the transition probabilities, corresponding to the $(v_3', 0)$ transitions when v_3' is an odd integer all vanish, and that for a linear model, in addition to these, all integrals pertaining to the $(v_2', 0)$ transitions when v_2' is an odd integer become zero. These results are, however, not to be interpreted as selection rules; they are simply consequences of the assumption of particular force fields. The results have been discussed in connection with the band intensities of ClO_2. It is shown that a knowledge of the structure of the excited molecule is essential to test quantitatively the results of the present work.

INTRODUCTION

As is well known, the relative intensities of bands in a band system are determined jointly by the initial distribution of molecules among the vibrational states and by the transition probabilities. The first factor depends, in emission, on experimental conditions such as temperature, pressure, mode of excitation, etc., and, in absorption, on the Boltzmann factor. In the following work we shall primarily be concerned with the transition probabilities in the absorption process at ordinary temperatures.

Based on Franck's theory of photochemical activity of molecules, Condon[1] has shown that the intensity distribution is definitely connected with the relative forms of $U'(r)$ and $U''(r)$ curves, and that in general there will be two or more most probable transitions for a given value of v' and v''. He has also shown how the wave mechanics predicts the small but nonvanishing values of the transition probabilities outside the classical motion.

While many applications have been made to spectra of diatomic molecules, particularly absorption spectra, this principle has not as yet been applied in detail to polyatomic molecules. Recently Urey and Johnston[2] have found that the intensity distribution in the band system of ClO_2 satisfies qualitatively the Franck-Condon rule, but, as the writer has elsewhere[3] pointed out, their analysis cannot be entirely correct and any improper correlation of the fundamental frequencies with the characteristic vibrations might vitiate their conclusions.

Despite our meager knowledge as regards the theory of electronic band spectra of polyatomic molecules and the acutal forces that govern the nuclear motion of a complicated molecule, it might be of interest to question what sort of intensity distribution is to be expected from an extension of the Franck-Condon principle. In the present paper, we shall consider only molecules of the general type XY_2 and two special cases which occur when the three atoms are equal and when the three atoms lie along a straight line.

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[1] Condon, Phys. Rev. **28**, 1182 (1926); Proc. Nat. Acad. Sci. **13**, 462 (1927); Phys. Rev. **32**, 858 (1928).

[2] Urey and Johnston, Phys. Rev. **38**, 2131 (1931).

[3] The preceding paper, Ku, Phys. Rev. **44**, 376 (1933).

AN EXTENSION OF THE FRANCK-CONDON THEORY

For simplicity we shall assume that the atoms lie in a plane in the form of an isosceles triangle with the X atom at the apex. Let us introduce a set of coordinates q, x, y, and α to specify the molecular configuration, q being the relative displacement of the two Y atoms, x and y, the displacements of the X atom relative to the center of gravity of the Y atoms, and α the half angle at the apex of the isosceles triangle. To a first approximation, when the forces are assumed to be central about each atom* and the amplitudes of vibration are taken to be infinitesimal compared to the nuclear distances in equilibrium, the potential and kinetic energies expressed in the normal coordinates take the following simple form:

$$V=\tfrac{1}{2}(\lambda_1\xi_1^2+\lambda_2\xi_2^2+\lambda_3\xi_3^2),\qquad T=\tfrac{1}{2}(\dot{\xi}_1^2+\dot{\xi}_2^2+\dot{\xi}_3^2),$$

in which the ξ's are obtained from the following transformation:

$$q=a_1\xi_1+a_2\xi_2,\qquad y=b_1\xi_1+b_2\xi_2,\qquad x=c\xi_3,\tag{1}$$

and the coefficients are given by

$$a_1=\frac{2}{m}\left(\frac{K+\frac{1}{2}K'\sin^2\alpha-\frac{1}{2}m\lambda_2}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},\qquad a_2=\frac{2}{m}\left(\frac{\frac{1}{2}m\lambda_1-K-\frac{1}{2}K'\sin^2\alpha}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$b_1=-\frac{1}{m\mu^{\frac{1}{2}}}\left(\frac{\frac{1}{2}m\lambda_1-K-\frac{1}{2}K'\sin^2\alpha}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},\qquad b_2=\frac{1}{m\mu^{\frac{1}{2}}}\left(\frac{K+\frac{1}{2}K'\sin^2\alpha-\frac{1}{2}m\lambda_2}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$c=[2m\mu(1+\mu\cot^2\alpha)]^{-\frac{1}{2}},$$

where K and K' are the force constants, m and M the masses of the X and Y atoms, respectively, and λ's the three roots of the characteristic determinant[4]

$$\left[\left(\frac{m\lambda}{K'}\right)^2-2\left(\gamma+\frac{1}{2}+\frac{m}{M}\cos^2\alpha\right)\frac{m\lambda}{K'}+\frac{2\gamma}{\mu}\cos^2\alpha\right]\left[\frac{m\lambda}{K'}-1-\frac{2m}{M}\sin^2\alpha\right]=0,$$

where $\gamma=K/K'$, $\mu=M/(2m+M)$.

Evidently the vibratory motion of the system may be regarded as the motions of three independent equivalent harmonic oscillators with frequencies $\nu_i=\lambda_i^{\frac{1}{2}}/2\pi$. Now the motion of the ith simple harmonic oscillator expressed in the action and angle variables is given by

$$P_i=(2\mu_i\nu_iJ_i)^{\frac{1}{2}}\cos 2\pi W_i,\qquad \xi_i=(1/2\pi)(2J_i/\mu_i\nu_i)^{\frac{1}{2}}\sin 2\pi W_i.$$

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[4] Dennison, Phil. Mag. **1**, 195 (1926).

* This restriction is in fact not necessary, for if we, with Yates[5] assume that the force tending to restore a particle after a displacement is the sum of two types, the first acting along the line XY and obeying Hooke's law, the second, an angular restoring force, acting at right angles to the first and proportional to the arc displacement of the Y's the characteristic determinant now takes the following form:

$$\left[\frac{\lambda m}{k'}-1-\frac{2m}{M}\sin^2\alpha\right]\left[\left(\frac{\lambda m}{k'}\right)^2-2\left(\frac{1}{2}+\frac{m}{M}\cos^2\alpha+\frac{\gamma}{\mu}\sin^2\alpha\right)\frac{\lambda m}{k}+\frac{2\gamma}{\mu}\right]=0$$

and the coefficients in Eqs. (1) become

$$a_1=\frac{2}{m}\left(\frac{K\cos^2\alpha+\frac{1}{2}K'\sin^2\alpha-\frac{1}{2}m\lambda_2}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$a_2=\frac{2}{m}\left(\frac{\frac{1}{2}m\lambda_1-K\cos^2\alpha-\frac{1}{2}K'\sin^2\alpha}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$b_1=-\frac{1}{m\mu^{\frac{1}{2}}}\left(\frac{\frac{1}{2}m\lambda_1-K\cos^2\alpha-\frac{1}{2}K'\sin^2\alpha}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$b_2=\frac{1}{m\mu^{\frac{1}{2}}}\left(\frac{K\cos^2\alpha+\frac{1}{2}K'\sin^2\alpha-\frac{1}{2}m\lambda_2}{\lambda_1-\lambda_2}\right)^{\frac{1}{2}},$$

$$c=\frac{1}{[2m\mu(1+\mu\cot^2\alpha)]^{\frac{1}{2}}}.$$

[5] Yates, Phys. Rev. **36**, 555 (1930).

Following Condon we shall assume that the transition occurs instantaneously and that the motion of the massive nuclei is unaffected during the transition, then the following conditions must be satisfied:

$$q'=q''+q_0,\quad y'=y''+y_0,\quad x'=x'',\quad p_q'=p_q'',\quad p_y'=p_y'',\quad p_x'=p_x'',$$

where q_0 and y_0 denote the change in the nuclear distances of the normal configuration. Referring to Eqs. (1) we can immediately write down the following set of equations:

$$\frac{a_1'}{2\pi}\left(\frac{2J_1'}{\nu_1'}\right)^{\frac{1}{2}}\sin 2\pi W_1'+\frac{a_2'}{2\pi}\left(\frac{2J_2'}{\nu_2'}\right)^{\frac{1}{2}}\sin 2\pi W_2'=q_0+\frac{a_1}{2\pi}\left(\frac{2J_1}{\nu_1}\right)^{\frac{1}{2}}\sin 2\pi W_1+\frac{a_2}{2\pi}\left(\frac{2J_2}{\nu_2}\right)^{\frac{1}{2}}\sin 2\pi W_2,$$

$$a_1'(2\nu_1'J_1')^{\frac{1}{2}}\cos 2\pi W_1'+a_2'(2\nu_2'J_2')^{\frac{1}{2}}\cos 2\pi W_2'=a_1(2\nu_1J_1)^{\frac{1}{2}}\cos 2\pi W_1+a_2(2\nu_2J_2)^{\frac{1}{2}}\cos 2\pi W_2,\ \text{etc.},$$

all double primes which refer to the lower state being dropped for the sake of convenience.* Solving for J_i' in terms of J_i and W_i by eliminating W_i', writing θ_i for $2\pi W_i$ and replacing J_i by v_ih, we obtain

$$\begin{aligned}
v_1'=&A_1+B_1\sin\theta_1(v_1)^{\frac{1}{2}}+C_1\sin\theta_2(v_2)^{\frac{1}{2}}+D_1v_1+E_1v_2+F_1\cos 2\theta_1v_1+G_1\cos 2\theta_2v_2\\
&+H_1\sin\theta_1\sin\theta_2(v_1v_2)^{\frac{1}{2}}+I_1\cos\theta_1\cos\theta_2(v_1v_2)^{\frac{1}{2}},\\
v_2'=&A_2+B_2\sin\theta_1(v_2)^{\frac{1}{2}}+C_2\sin\theta_2(v_2)^{\frac{1}{2}}+D_2v_1+E_2v_2+F_2\cos 2\theta_2v_2+G_2\cos 2\theta_2v_2\\
&+H_2\sin\theta_1\sin\theta_2(v_1v_2)^{\frac{1}{2}}+I_2\cos\theta_1\cos\theta_2(v_1v_2)^{\frac{1}{2}},\\
v_3'=&D_3v_3+F_3\cos 2\theta_3v_3,
\end{aligned}\tag{2}$$

where

$$A_1=(2\pi^2\nu_1'/ha^2)(b_2'q_0-a_2'y_0)^2,\qquad A_2=(2\pi^2\nu_2'/ha^2)(b_1'q_0-a_1'y_0)^2,$$

$$B_1=(2/a^2)(b_2'q_0-a_2'y_0)(a_1b_2'-b_1a_2')(2\pi^2\nu_1'^2/h\nu_1)^{\frac{1}{2}},$$

$$B_2=(2/a^2)(b_1'q_0-a_1'y_0)(a_1b_1'-b_1a_1')(2\pi^2\nu_2'^2/h\nu_1)^{\frac{1}{2}},$$

$$C_1=(2/a^2)(b_2'q_0-a_2'y_0)(a_2b_2'-b_2a_2')(2\pi^2\nu_1'^2/h\nu_2)^{\frac{1}{2}},$$

$$C_2=(2/a^2)(b_1'q_0-a_1'y_0)(a_2b_1'-b_2a_1')(2\pi^2\nu_2'^2/h\nu_2)^{\frac{1}{2}},$$

$$D_1=(1/2a^2)(a_1b_2'-b_1a_2')^2(\nu_1/\nu_1'+\nu_1'/\nu_1),$$

$$D_2=(1/2a^2)(a_1b_1'-b_1a_1')^2(\nu_1/\nu_2'+\nu_2'/\nu_1),$$

$$D_3=\tfrac{1}{2}(\nu_3/\nu_3'+\nu_3'/\nu_3),$$

$$E_1=(1/2a^2)(a_2b_2'-b_2a_2')^2(\nu_2/\nu_1'+\nu_1'/\nu_2),$$

$$E_2=(1/2a^2)(a_2b_1'-b_2a_1')^2(\nu_2/\nu_2'+\nu_2'/\nu_2),$$

$$F_1=(1/2a^2)(a_1b_2'-b_1a_2')^2(\nu_1/\nu_1'-\nu_1'/\nu_1),$$

$$F_2=(1/2a^2)(a_1b_1'-b_1a_1')^2(\nu_1/\nu_2'-\nu_2'/\nu_1),$$

$$F_3=\tfrac{1}{2}(\nu_3/\nu_3'-\nu_3'/\nu_3),$$

$$G_1=(1/2a^2)(a_2b_2'-b_2a_2')^2(\nu_2/\nu_1'-\nu_1'/\nu_2),$$

$$G_2=(1/2a^2)(a_2b_1'-b_2a_1')^2(\nu_2/\nu_2'-\nu_2'/\nu_2),$$

$$H_1=(2/a^2)(a_1b_2'-b_1a_2')(a_2b_2'-b_2a_2')(\nu_1'^2/\nu_1\nu_2)^{\frac{1}{2}},$$

$$H_2=(2/a^2)(a_1b_1'-b_1a_1')(a_2b_1'-b_2a_1')(\nu_2'^2/\nu_1\nu_2)^{\frac{1}{2}},$$

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* For the same reason all double primes shall be omitted throughout the following discussion.

$$I_1=(2/a^2)(a_1b_2'-b_1a_2')(a_2b_2'-b_2a_2')(\nu_1\nu_2/\nu_1'^2)^{\frac{1}{2}},$$

$$I_2=(2/a^2)(a_1b_1'-b_1a_1')(a_2b_1'-b_2a_1')(\nu_1\nu_2/\nu_2'^2)^{\frac{1}{2}},$$

$$a^2=(a_1'b_2'-a_2'b_1')=1/m^2\mu.$$

Supposing the electronic transition to be independent of the phase of motion, it is easy to see that the values of v_i' corresponding to the small values of $\partial v_i/\partial\theta_i$ will be strongly weighted. Consequently, the most probable values of v_i' are obtained by substituting in Eqs. (2) the values of θ_i satisfying

$$\partial v_1'/\partial\theta_1=\partial v_1'/\partial\theta_2=\partial v_2'/\partial\theta_1=\partial v_2'/\partial\theta_2=\partial v_3'/\partial\theta_3=0.$$

We finally obtain

$$\begin{aligned} v_1' &= \begin{cases} A_1\pm B_1(v_1)^{\frac{1}{2}}\pm C_1(v_2)^{\frac{1}{2}}+D_1v_1+E_1v_2-F_1v_1-G_1v_2+H_1(v_1v_2)^{\frac{1}{2}} \\ A_1\pm B_1(v_1)^{\frac{1}{2}}\mp C_1(v_2)^{\frac{1}{2}}+D_1v_1+E_1v_2-F_1v_1-G_1v_2-H_1(v_1v_2)^{\frac{1}{2}} \end{cases} \\ v_2' &= \begin{cases} A_2\pm B_2(v_1)^{\frac{1}{2}}\pm C_2(v_2)^{\frac{1}{2}}+D_2v_1+E_2v_2-F_2v_1-G_2v_2+H_2(v_1v_2)^{\frac{1}{2}} \\ A_2\pm B_2(v_1)^{\frac{1}{2}}\mp C_2(v_2)^{\frac{1}{2}}+D_2v_1+E_2v_2-F_2v_1-G_2v_2-H_2(v_1v_2)^{\frac{1}{2}} \end{cases} \\ v_3' &= \begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3. \end{cases} \end{aligned} \tag{3}$$

We notice that there are, in general, four most probable values of v_1' and v_2' corresponding to any set of v_1 and v_2. This interdependence is one of the consequences of the character of vibration, the coordinates q and y being functions of ξ_1 and ξ_2. On the other hand, x is a function of ξ_3 alone and hence v_3' varies independently. We further notice that in the absorption process when $v_1=v_2=v_3=0$, Eqs. (3) are reduced to $v_1'=A_1$, $v_2'=A_2$, $v_3'=0$. While the values of A_1 and A_2 are explicitly given on page 385, it is more convenient for later discussion to write

$$v_1'=\tfrac{1}{2}m^2\mu\alpha_1'(b_2'q_0-a_2'y_0)^2, \qquad v_2'=\tfrac{1}{2}m^2\mu\alpha_2'(b_1'q_0-a_1'y_0)^2, \tag{4}$$

where

$$\alpha_1'=4\pi^2\nu_1'/h, \qquad \alpha_2'=4\pi^2\nu_2'/h.$$

Here the α's may be regarded as the amplitudes of the nuclear vibration in terms of the normal frequencies, and the a's and b's the amplitude of the component displacements of the nuclei. It has been found that there exists a simple relation between the most probable values of v_1' and v_2' given by

$$v_1'/\nu_1'+v_2'/\nu_2'=(2m/h)(q_0^2+4\mu y_0^2). \tag{5}$$

We may then conclude that in the absorption process at ordinary temperatures the strongest bands in the v_1' and v_2' progressions will be (v_1', 0) and (v_2', 0) where v_1' and v_2' are associated with the quantized states in the neighborhood of the unquantized ones determined by A_1 and A_2. It is clear that if there be small change in the normal moment of inertia caused by the electron jump approaching the case $q_0=y_0=0$, the most probable transitions would be the (0, 0) bands. The strongest band in the v_3' progression is, however, always (0, 0).

Consider a special case which occurs when the three atoms become equal. Referring to the characteristic determinant on page 384 we obtain

$$\nu_1=(1/2\pi)(3K'/m)^{\frac{1}{2}}, \qquad \nu_2=\nu_3=\nu_1/2^{\frac{1}{2}}.$$

The coefficients in Eqs. (1) now become

$$a_1=a_2=1/m^{\frac{1}{2}}, \qquad b_1=b_2=-(3/4m)^{\frac{1}{2}}, \qquad c=(3/4m)^{\frac{1}{2}}.$$

The most probable transitions are found to be

$$v_i' = A_i \pm B_i(v_i)^{\frac{1}{2}} + (D_i - F_i)v_i, \quad \text{for} \quad |B_i/(4F(v_i)^{\frac{1}{2}})| > 1,$$

and in addition to these

$$v_i' = A_i + B_i^2/8F_i + (D_i + F_i)v_i, \quad \text{for} \quad |B_i/(4F_i(v_i)^{\frac{1}{2}})| < 1, \qquad i = 1, 2 \quad (6)$$

$$v_3' = \begin{cases} (\nu_3/\nu_3')v_3, \\ (\nu_3'/\nu_3)v_3, \end{cases}$$

where

$$A_1 = (\pi^2 m\nu_1'/18h)q_0^2, \qquad A_2 = (25\pi m\nu_2'/18h)q_0^2,$$

$$B_1 = (\pi/3)(2m/h\nu_1)^{\frac{1}{2}}\nu_1' q_0, \qquad B_2 = (5\pi/3)(2m/h\nu_2)^{\frac{1}{2}}\nu_2' q_0,$$

$$D_1 = \tfrac{1}{2}(\nu_1/\nu_1' + \nu_1'/\nu_1), \qquad D_2 = \tfrac{1}{2}(\nu_2/\nu_2' + \nu_2'/\nu_2),$$

$$F_1 = \tfrac{1}{2}(\nu_1/\nu_1' - \nu_1'/\nu_1), \qquad F_2 = \tfrac{1}{2}(\nu_2/\nu_2' - \nu_2'/\nu_2).$$

The distinction between v_2' and v_3' vanishes because of the degeneracy.

The vibrations of a collinear model have been discussed fully by Dennison.[6] The method of finding the transition probabilities are very much the same as has already been sketched above and need not be repeated here. We shall simply give the most probable values of the v's as follows:

$$v_1' = a_1 + (b_1 - d_1)v_1 - c_1(v_1)^{\frac{1}{2}}, \quad \text{when} \quad |c_1/(4d_1(v_1)^{\frac{1}{2}})| > 1,$$

and in addition to these

$$v_1' = a_1 + c_1/8d_1 + (b_1 + d_1)v_1, \quad \text{when} \quad |c_1/(4d_1(v_1)^{\frac{1}{2}})| < 1,$$

where

$$a_1 = (\pi^2 m\nu_1'/h)q_0^2, \qquad b_1 = \tfrac{1}{2}(\nu_1/\nu_1' + \nu_1'/\nu_1),$$

$$c_1 = 2\pi\nu_1'(m/h\nu_1)^{\frac{1}{2}}q_0, \qquad d_1 = \tfrac{1}{2}(\nu_1/\nu_1' + \nu_1'/\nu_1);$$

$$v_2' = \tfrac{1}{2}(\nu_2/\nu_2' + \nu_2'/\nu_2)v_2 \pm K(\nu_2/\nu_2' - \nu_2'/\nu_2);$$

where K stands for $\cos 2\pi(\delta_z - \delta_y)$, δ_z and δ_y being the phase angle of the component harmonic vibrations of the isotropic plane oscillator. A special case occurs when the component harmonic vibrations are in phase ($\delta_z = \delta_y$), Eqs. (7) are reduced to

$$v_2' = \begin{cases} 3/2(\nu_2/\nu_2')v_2 \\ 3/2(\nu_2'/\nu_2)v_2; \end{cases} \qquad v_3' = \begin{cases} (\nu_3/\nu_3')v_3 \\ (\nu_3'/\nu_3)v_3. \end{cases}$$

The above analysis leads to the following conclusions: In the absorption process at ordinary temperatures the most intense band in the v_1' progression will be $v_1' = a_1$; the larger the change in the normal equilibrium distance between the Y's the higher will be the value of v_1'. The strongest band in the v_2' progression depends on the phase difference of the component harmonic vibrations as well as the characteristic frequencies in both states. The most intense band in the v_3' progression will again be (0, 0).

Intensity Distribution According to Wave Mechanics

The same problem will now be considered from the wave mechanical standpoint. According to the usual method for calculating transition probabilities, the matrix component of the electric moment of the molecule corresponding to the transition in question must be computed. Born and Oppenheimer[7] have shown how the general wave equation can be handled. On account of the heavy mass of the nuclei as compared with that of the electrons the complete wave function of a

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[6] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[7] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927).

molecule in a state characterized by the electronic quantum number e and the vibrational quantum number v may be approximately written

$$\psi_{ev}(x,\ \xi)=\phi_e(x,\ \xi)u_{ev}(\xi),$$

where ϕ_e is the wave function of electronic motion, and u_{ev} is that of nuclear vibration, x and ξ being the collective coordinates of the electrons and nuclei respectively.

Since the nuclear motion of a symmetrical triatomic molecule may be resolved into that of three independent equivalent oscillators the vibrational factor of the wave function, to a first approximation, can be written

$$u_{ev}(\xi)=\Pi u_{ev}\ (\xi_i).$$

The electric moment $M(x,\ \xi)$ of the molecule is a linear function of the electronic and nuclear coordinates, and the matrix component of electric moment whose square measures the transition probability of an electronic transition $(e',\ e)$ and vibrational transition $(v',\ v)$ is

$$M\begin{pmatrix} e' & e \\ v' & v \end{pmatrix}=M(x,\ \xi)\psi_{e'v'}(x,\ \xi)\psi_{ev}(x,\ \xi)d\xi.$$

When studying the intensity distribution in a band system we shall deal with the same electronic transition. Suppose we integrate over the electronic coordinates, then we have

$$M_{v'v}=M_{e'e}(\xi)u_{v'}(\xi)u_v(\xi)d\xi.$$

As ordinarily the wave functions vary with the nuclear coordinates much more rapidly than does the electric moment and the latter does not change very much over the region in which the wave functions have appreciable values, it becomes clear that for low values of v all but the constant term in $M_{e'e}(\xi)$ may be neglected. Writing $M_{e'e}(\xi)=A$ we have

$$M_{v'v}=a\Pi u_{v'}(\xi_i)u_v(\xi_i)d\xi_i.$$

If $u_{v_i'}(\xi_i)=(1/N_{v_i'})H_{v_i'}(\eta_i')e^{-\eta_i'^2}$ is taken to be the wave function of the nuclear motion for the upper state,

$$u_{v_i}(\xi_i)=(1/N_{v_i})H_{v_i}(\beta_i\eta_i'+\zeta_i)e^{-\frac{1}{2}(\beta_i\eta'_i+\zeta_i)^2}$$

then represents that for the lower state, where

$$\eta_i=\alpha_i^{\frac{1}{2}}\xi_i,\quad \alpha_i=2\pi(\lambda_i)^{\frac{1}{2}}/h,\quad \beta_i=(\nu_i/\nu_i')^{\frac{1}{2}},$$

$$\zeta_i=\alpha_i^{\frac{1}{2}}(\xi_{ei}'-\xi_{ei}),\quad N_{v_i}=\pi^{\frac{1}{4}}2^{v_i/2}(v_i\,!)^{\frac{1}{2}}$$

ξ_i being the normal coordinates of nuclei in the equilibrium configuration, H_{v_i} the Hermitian functions associated with the state specified.

The portion contributed by the ith oscillator will be

$$M_{v_i'v_i}=\frac{1}{N_{v_i'}N_{v_i}}\int H_{v_i'}(\eta_i')e^{-\eta_i'^2/2}H_{v_i}(\beta_i\eta_i'+\zeta_i)e^{-\frac{1}{2}(\beta_i\eta'_i+\zeta_i)^2}d\eta_i'. \tag{7}$$

If we study the absorption spectrum at a room temperature we shall primarily be interested in transition probabilities associated with bands originating from the lowest state, i.e., $v_i=0$. For these transitions the integral may be evaluated quite easily. It may be shown that the matrix elements corresponding to the transitions $(v_3',\ 0)$ when v_3' is an odd integer all vanish, while all others take on values depending on the ratio of the normal frequencies and molecular constants characteristic for the transition in question. The same statement holds for the case in which the three atoms become equal.

For a collinear model the integral which measures the transition probability is approximately

$$M_{v'v}=B\int u_{e'v'_1}(q)u_{ev_1}(q)u_{e'v'_2}(r,\ \phi)u_{ev_2}(r,\ \phi)u_{e'v'_3}(x)u_{ev_3}(x)dq\,dr\,d\phi\,dx,$$

where B is a constant representing the effective electric moment of the molecule for the electronic transition in question and

$$u_{v_1}=(1/N_{v_1})H_{v_1}(\rho_1)e^{-\rho_1^2/2},$$

$$u_{v_2}=\rho_2^{|m|}\sum_{k=0}^{v_2-m} a_k\rho_2^k e^{-\rho_2^2/2}e^{+im\phi},$$

$$u_{v_3}=(1/N_{v_3})H_{v_3}(\rho_3)e^{-\rho_3^2/2},$$

$$\rho_1=\pi\overline{(2m\nu_1/h)}^{\frac{1}{2}}q,\qquad \rho_2=2\pi\overline{(\mu\nu_2/h)}^{\frac{1}{2}}r,$$

$$\rho_3=2\pi\overline{(\mu\nu_3/h)}^{\frac{1}{2}}x,\qquad a_{k+2}=\frac{2k+2m-2v_2}{(k+2)(k+2m+2)}a_k.$$

It can be shown that the integrals corresponding to the transitions $(v_2', 0)$ or $(v_3', 0)$ when v_2' or v_3' is an odd integer all vanish and all other integrals may be expressed in terms of the normal frequencies and molecular constants.

Perhaps it should be emphasized that the vanishing of the matrix components representing transition probabilities as mentioned above is not to be interpreted as rigid selection rules. We have shown that on the assumption of any particular force fields—whether it be central or valence forces—we are led to deal with wave functions (e.g., Hermitian polynomials, functions containing a factor $e^{im\phi}$ where m is an integer positive or negative, etc.) whose properties are directly responsible for the vanishing integrals. As in an actual molecule, particularly when transitions to some high vibrational states are involved, the force fields might deviate considerably from what has been assumed, we would, therefore, rather expect some of the forbidden transitions to appear in the spectrum.

The Intensities of the ClO$_2$ Bands

In the preceding paper[3] we have mentioned the remarkable uniformity in the intensity distribution of the ClO$_2$ bands. In practically all the progressions there are central maxima which occur in the neighborhood of 3360A. This general feature was reported by Urey and Johnston[2] who have plotted curves showing the distribution of intensities in the four most prominent v_2' progressions. The overlapping of bands makes the intensity measurement rather difficult. We have estimated the relative intensities from the microphotometer records. These estimates have been made at points of maximum intensity in the unresolved bands and no corrections have been attempted for the variations of the dispersion of the instrument and of the plate sensitivity with the wave-length. The results are shown in Figs. 1 and 2 where the intensities in arbitrary unit are plotted against v_2'.

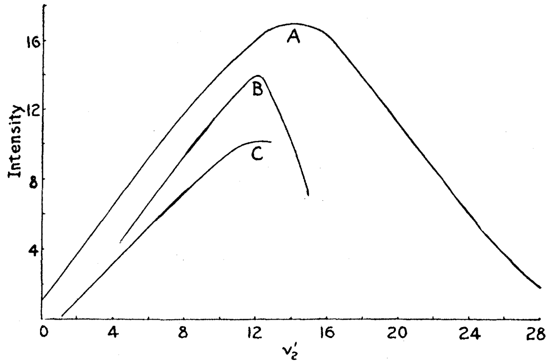

FIG. 1. A. $(0, v_2', 0)\leftarrow(0, 0, 0)$; B. $(0, v_2', 0)\leftarrow(1, 0, 0)$; C. $(0, v_2', 0)\leftarrow(0, 0, 1)$.

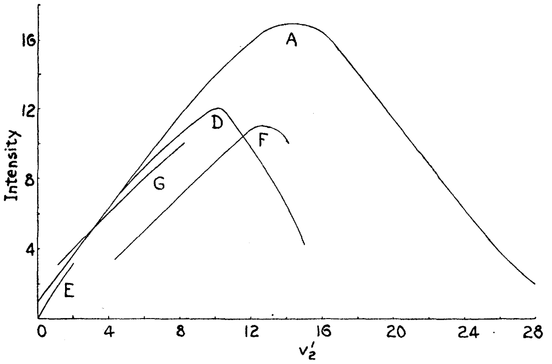

FIG. 2. A. $(0, v_2', 0)\leftarrow(0, 0, 0)$; D. $(1, v_2', 0)\leftarrow(0, 0, 0)$; E. $(0, v_2', 1)\leftarrow(0, 0, 0)$; F. $(1, v_2', 1)\leftarrow(0, 0, 0)$; G. $(2, v_2', 1)\leftarrow(0, 0, 0)$.

We are now ready to discuss how far the observed intensities agree with the results of the present analysis. On the whole, because of the Boltzmann factor, we would expect the bands originating from the (0, 0, 0) level to be much stronger than the corresponding bands arising from any of the higher levels, and this has been found to be consistent with the vibrational analysis to which reference has been made. Let us assume, for the moment, our vibrational analysis to be correct and let us examine each mode of vibration independently. The absence of all bands associated with transitions to v_3' higher than 1 and the fact that the corresponding members of (1, 0) are considerably weaker than those of (0, 0) seem to support the theoretical prediction that the (0, 0) transition in the (v_3', 0) progression is most favorable. On the other hand, the nonvanishing intensity of the (1, 0) transition would mean that our wave mechanical treatment is inadequate and that higher orders of approximation must be employed in order to account for the observed intensity.

The intensities in the v_1' progression may be examined by comparing the corresponding members of (0, v_2', 0) with those of (1, v_2', 0) or (0, v_2', 1) with (1, v_2', 1), and (2, v_2', 0), all originating from the ground state. Here too all transitions to v_1' higher than 2 are absent. We notice that, for $v_3'=0$, the corresponding members of the (1, 0) bands are much less intense than those of the (0, 0) bands; for $v_3'=1$, this becomes less obvious. The most probable value of v_1' therefore remains uncertain.

If we substitute in Eqs. (4) the value of the molecular constants as given in Table V of the preceding paper we obtain

$$v_1'=8.93\times10^{16}(1.25q_0-2.08y_0)^2,$$

$$v_2'=23.8\times10^{16}(-1.44q_0-1.81y_0)^2.$$

With a knowledge of the most probable values of v_1 and v_2 it would seem possible to solve for q_0 and y_0—the change in the nuclear distances in the normal equilibrium configuration—and consequently to calculate the dimensions of the excited molecule. We have seen in Fig. 1 that the most intense band in the (0, v_2, 0) (0, 0, 0) progression is $v_2'=14$ or 15. Unfortunately the most probable value of v_1' is not precisely known. Until we have known the values of y_0 and q_0 we cannot make use of Eqs. (3)–(6) to test quantitatively the results of the present work.

I wish to express my gratitude to Professor D. M. Dennison for his continued interest in the work and frequent discussions throughout the investigation.