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BAND SPECTRA INTENSITIES FOR SYMMETRICAL DIATOMIC MOLECULES

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Abstract

The intensity of a spectral line may be calculated in the new quantum mechanics by evaluating the integral of the product of the electric moment and the wave functions of the initial and of the final states. The complete wave function may be written approximately as a product of a nuclear wave function and an electronic wave function. Furthermore, the electric moment can be approximately written as the sum of a function of the nuclear coordinates only and a function of the electronic coordinates only. For symmetrical diatomic molecules the term in the electric moment which is a function of the nuclear coordinates only is zero so that the intensity integral reduces to a double integral which may be written as a product of an electronic integral and a nuclear integral. The electronic integral is constant for all the lines corresponding to the same electronic transition and the integrand of the nuclear integral consists only of the product of the radial wave functions for the initial and the final states. The integration of the nuclear integral is carried out using harmonic oscillator wave functions whose origins are shifted due to the change of the nuclear separation during the electronic transition.

A comparison is made between the intensities calculated in the above manner and those obtained by experiment. In the case of Na_2 good quantitiative agreement is obtained between the experimental and the calculated results. Accurate values of the moments of inertia in the initial and final states are not known for K_2 but it is possible to show that if a value of the change in the nuclear separations during the transition is assumed, agreement is possible for all of the lines corresponding to low quantum numbers. Good qualitative agreement is obtained for I_2. Calculations are made for the absorption spectra and the $3'B-2'S$ emission band system of H_2 but the agreement in these cases is not as good as for Na_2 and K_2.

I. Introduction

On THE basis of the old quantum theory Condon[1] was able to show that in connection with a given electronic transition in a diatomic molecule certain transitions were more probable than others. His calculations were based upon Franck's[2] assumption that during an electronic transition nuclei which are originally in a non-vibrating state remain momentarily fixed because of their large masses compared with those of the electrons. Since the equilibrium distance between the nuclei is altered due to the motion of the electrons, the nuclei acquire a potential energy with respect to the new equilibrium points and begin to vibrate. The amplitude of the vibration acquired after the transition is approximately equal to the change in the equilibrium

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[1] E. Condon, Phys. Rev. **28**, 1182 (1926).

[2] J. Franck, Trans. Faraday Society (1925).

separations, therefore it is possible for the most probable nuclear transition to be calculated.

If the nuclei are vibrating in the initial state then almost any amplitude in the end state is possible. A calculation similar to that mentioned above can be employed except that instead of focusing our attention on the equilibrium position in the initial state, we focus our attention on the positions in which the nuclei spend most of the time. These positions will naturally be the turning points of the vibratory motion. With potential energy diagrams to determine the turning points of the vibration Condon was able to show that the positions of maximum intensities in the well-known double entry tables lie along a parabolic path and agree fairly well with experiment. As Condon's theory is essentially only one of transition probabilities the distribution in the initial state is not included.[3]

In a second paper Condon[4] showed that the ideas expressed above on the basis of the old quantum theory could be carried over into the new quantum mechanics. In the new quantum mechanics the intensity of a spectral line may be calculated by evaluating the integral of the product of the electric moment and the wave functions of the initial and final states where the integration is carried out over all of the coordinates of the electrons and the nuclei. Thus a measure of the intensity is given by the expression (following Condon):

$$I = \int \int M(x, r)\psi_{e'n'}(x, r)\psi_{e''n''}(x, r)dxdr,$$

where M is the instantaneous electric moment, $\psi_{e'n'}$ and $\psi_{e''n''}$ are the wave functions of the initial and final states, x and r are total coordinates of the electron and of the nuclei respectively and e and n are electronic and vibrational quantum numbers. According to the work of Born and Oppenheimer[5] the complete wave function ψ_{en} can be approximately expressed as a product of an electronic wave function $\Phi_e(x)$ and an oscillatory wave function $\Psi_{en}(r)$. The latter function corresponds to the motion of the nuclei moving under an effective force arising from the moving electrons and the repulsion of the nuclei. We may write our integral:

$$I = \int \int M(x, r)\Phi_{e'}(x)\Psi_{e'n'}(r)\Phi_{e''}(x)\Psi_{e''n''}(r)dxdr.$$

The electric moment is defined as the vector sum of the coordinates of the electrons times their charge and the coordinates of the nuclei times their charge. This may be approximately expressed in the following way:

$$M(x, r) = A(x) + B(r)$$

because during the transition of the electrons the nuclei remain practically fixed and the first term (representing the vector sum of the electronic charges

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[3] Cf. G. Herzberg, Zeits. f. Physik **49**, 761 (1928).

[4] E. Condon, Phys. Rev. **32**, 858 (1928).

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

times x) will be a constant over the integration of the electron coordinates. The second term (representing the vector sum of the nuclear charge times r) will be a function of only the nuclear coordinates because the heavy nuclei cannot respond immediately to the changes in the electronic arrangement. We have therefore:

$$I = \int A(x)\Phi_{e'}(x)\Phi_{e''}(x)dx \int \Psi_{e'n'}(r)\Psi_{e''n''}(r)dr + \int \Phi_{e'}(x)\Phi_{e''}(x)dx \int B(r)\Psi_{e'n'}(r)\Psi_{e''n''}(r)dr.$$

The integrals involving the electron coordinates will be constant for a given electronic transition so that

$$I = C_1 \int \Psi_{e'n'}(r)\Psi_{e''n''}(r)dr + C_2 \int B(r)\Psi_{e'n'}(r)\Psi_{e''n''}(r)dr.$$

This integral cannot be evaluated in general because we do not know the ratio of the constants ($B(r)$ is probably a linear function). However if we restrict ourselves to symmetrical diatomic molecules the nuclear electric moment will always be zero so that the last term drops out and we have only

$$I = C_1 \int \Psi_{e'n'}(r)\Psi_{e''n''}(r)dr. \tag{1}$$

It is the purpose of this paper to evaluate this integral and to compare the results with experiment in several cases.

II. Intensities for Harmonic Oscillations

The approximate wave equation for the nuclear motions of the diatomic molecule may be written

$$\nabla^2\Psi + \frac{8\pi^2\mu}{h^2}\left[W - \frac{Z^2e^2}{r} + V_e(r)\right]\Psi = 0 \tag{2}$$

where Ze is the charge on one of the nuclei, μ is the equivalent mass $(=M_1M_2/M_1+M_2)$, r is the separation of the nuclei and $V_e(r)$ is the mean potential energy due the electrons. The wave function may be separated into three functions in the usual manner by setting $\Psi = N\Phi(\phi)\ \Theta(\theta)\ R(r)/r$ where N is a normalizing factor. The equations in ϕ and θ will not have any effect[6] on the calculated intensities of the spectral lines and we may therefore pass immediately to the equation in r

$$\frac{d^2R}{dr^2} - \frac{m(m+1)}{r^2}R + \frac{8\pi^2\mu}{h^2}\left[W - \frac{Z^2e^2}{r} + V_e(r)\right]R = 0 \tag{3}$$

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[6] A. Sommerfeld, Ergänzungsband, p. 69.

where m is the rotational quantum number. Making the substitution $\rho = r/r_0$ (r_0 = equilibrium separation of the nuclei) we obtain

$$R'' + \left[\frac{8\pi^2 J_0}{h^2}(W - f(\rho)) - \frac{m(m+1)}{\rho^2}\right] R = 0 \tag{4}$$

in which $J_0 = \mu r_0^2$ and $f(\rho)$ represents the effective potential energy.

In this paper we will restrict ourselves to linear oscillations and we may therefore put $f(\rho) = -D + [(2\pi\nu_0)^2 J_0/2]\,\xi^2$ where $\xi = \rho - 1$ and D is the dissociation energy and ν_0 is the frequency of vibration for very small amplitudes. Making use of this expression in Eq. (4) and expanding ρ in terms of ξ (or, one could set $m = 0$) and finally making the substitution $\eta = 2\pi(\nu_0 J_0)^{1/2}/(h)^{1/2}\,\xi$, we obtain

$$R'' + \left[\frac{2}{h\nu_0}\left\{W + D - m(m+1)\frac{h^2}{8\pi^2 J_0}\right\} - \eta^2\right] R = 0 \tag{5}$$

which is the wave equation for the linear oscillator.[7]

The solution of this equation is well known and may be written

$$R_n = \frac{1}{N_n} e^{-\eta^2/2} H_n(\eta) \quad \text{and} \quad W + D - m(m+1)\frac{h^2}{8\pi^2 J_0} = \left[n + \frac{1}{2}\right] h\nu_0 \tag{6}$$

where n is the vibrational quantum number and $H_n(\eta)$ is a Hermitian polynominal.

We wish to evaluate the integral (1) which may now be written in terms of (ρ) and the radial wave function, in the following manner:

$$I = \text{const.} \int_0^\infty R_{e'n'}(\rho) R_{e''n''}(\rho) d\rho. \tag{7}$$

As far as the nuclei are concerned the effect of an electron transition is, that besides the change in the equilibrium positions of the nuclei there is also a change in the binding or potential energy such that the nuclei acquire a new vibration frequency after the transition. Therefore if we take $R_{e'n'} = (1/N_{n'}) e^{-\eta^2/2} H_{n'}(\eta)$ as the nuclear part of the wave function for the upper state, we will have for the lower state $R_{e''n''} = (1/N_{n''}) \exp - [(\alpha\eta + \delta)^2/2]\, H_{n''}(\alpha\eta + \delta)$ where α and δ represent respectively measures of the change in frequency and the change in equilibrium position. From the definition of η we see that

$$\eta = [2\pi(\nu_0' J_0')^{1/2}/(h)^{1/2} r_0] r - 2\pi(\nu_0' J_0')^{1/2}/(h)^{1/2}$$

so that

$$\begin{aligned} \alpha\eta + \delta = {} & [(\alpha 2\pi(\nu_0' J_0')^{1/2}/(h)^{1/2} r_0'][r + \delta r_0'(h)^{1/2}/2\pi\alpha(\nu_0' J_0')^{1/2}] \\ & - \alpha 2\pi(\nu_0' J_0')^{1/2}/(h)^{1/2} = [2\pi(\nu_0''\mu)^{1/2}/(h)^{1/2}] r - 2\pi(\nu_0''\mu)^{1/2} r_0''/(h)^{1/2}. \end{aligned}$$

Thus $\alpha = (\nu_0''/\nu_0')^{1/2}$ and

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

$$\delta = (r_0' - r_0'')2\pi(\nu_0''\mu)^{1/2}/(h)^{1/2} = 0.1221(r_0' - r_0'')(\nu_0''M)^{1/2}$$

where ν_0'' is expressed in cm^{-1}, M is the atomic weight (O = 16) of one of the atoms and $(r_0' - r_0'')$ is in Angstroms.

The integral (7) then becomes

$$I = \text{const} \int_{-\infty}^{+\infty} (N_{n'}N_{n''})^{-1} e^{-\eta^2/2} e^{-(\alpha\eta+\delta)^2/2} H_{n'}(\eta) H_{n''}(\alpha\eta + \delta)d\eta \tag{8}$$

where the limits are taken from $-\infty$ to $+\infty$ instead of from -1 to $+\infty$ since the addition of the region from -1 to $-\infty$ will not appreciably affect the value of the integral for small quantum numbers. The values of the normalizing factors are well known for the linear oscillator, being

$$N_{n'} = \left[2^{n'}n'!\pi^{1/2}h^{1/2}/2\pi(\nu_0'\mu)^{1/2}\right]^{1/2}$$

$$N_{n''} = \left[2^{n''}n''!\pi^{1/2}h^{1/2}/2\pi(\nu_0''\mu)^{1/2}\right]^{1/2} \tag{9}$$

In order to carry through the integration of Eq. (8) the method used by Schrödinger[8] in the Stark effect may be applied. The "erzeugende" function[9] for the Hermitian polynomial is

$$\sum_{n'=0}^{n'=\infty} \frac{H_{n'}(\eta)}{n'!} s^{n'} = e^{-s^2+2s\eta}$$

and for the function of the lower state

$$\sum_{n''=0}^{n''=\infty} \frac{H_{n''}(\alpha\eta + \delta)}{n''!} t^{n''} = e^{-t^2+2t(\alpha\eta+\delta)}.$$

If these expressions are multiplied together and also multiplied by the exponentials in Eq. (8) we have after integration

$$\begin{aligned}\sum_{n'=0}^{n'=\infty} \sum_{n''=0}^{n''=\infty} \frac{s^{n'}t^{n''}}{n'!n''!} \int_{-\infty}^{+\infty} & H_{n'}(\eta)H_{n''}(\alpha\eta + \delta)e^{-\eta^2/2}e^{-(\alpha\eta+\delta)^2/2}d\eta \\ &= \int_{-\infty}^{+\infty} e^{-s^2+2s\eta-\eta^2/2} e^{-t^2+2t(\alpha\eta+\delta)-(\alpha\eta+\delta)^2/2} d\eta \qquad (10) \\ &= \left(\frac{2\pi}{\alpha^2 + 1}\right)^{1/2} e^{-\delta^2/2(\alpha^2+1)} e^{[(s^2-t^2)(1-\alpha^2)-2\alpha\delta s+2\delta t+4\alpha st]/(1+\alpha^2)}.\end{aligned}$$

By expanding the last exponential factor in powers of s and t and then equating the like powers of s and t on both sides of the equation we obtain for the expression for the integral for each value of n' and n''. Making use of Eqs. (9), Eq. (8) becomes

$$\begin{aligned}&\int_{-\infty}^{+\infty} (N_{n'}N_{n''})^{-1} e^{-\eta^2/2} e^{-(\alpha\eta+\delta)^2/2} H_{n'}(\eta)\ H_{n''}(\alpha\eta + \delta)d\eta \\ &= C_3 \frac{(n'!n''!)^{1/2}}{2^{(n'+n'')/2}} \sum_{l=0}^{n' \text{ or } n''} \sum_{i=0}^{\substack{(n'-l)/2 \\ (n'-l-1)/2}} \sum_{j=0}^{\substack{(n''-l)/2 \\ (n''-l-1)/2}} a_{2l}b_{2i}c_{2j}d_{n'-2i-l}e_{n''-2j-l}\end{aligned} \tag{11}$$

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[8] E. Schrödinger, Ann. d. Physik **80**, 486 (1926).

[9] Courant and Hilbert, Methoden der mathematischen Physik I (Berlin 1924) p. 76.

where

$$C_3 = \left(\frac{h}{2\pi^2\mu\nu_0'\alpha(\alpha^2+1)}\right)^{1/2} e^{-\delta^2/2(\alpha^2+1)} \qquad a_{2l} = \frac{1}{l!}\left(\frac{4\alpha}{1+\alpha^2}\right)^l$$

$$b_{2i} = \frac{1}{i!}\left(\frac{1-\alpha^2}{1+\alpha^2}\right)^i \qquad c_{2j} = \frac{1}{j!}\left(\frac{-(1-\alpha^2)}{1+\alpha^2}\right)^j$$

$$d_{n'-2i-l} = \frac{1}{(n'-2i-l)!}\left(\frac{-2\alpha\delta}{1+\alpha^2}\right)^{(n'-2i-l)}$$

$$e_{n''-2j-l} = \frac{1}{(n''-2j-l)!}\left(\frac{2\delta}{1+\alpha^2}\right)^{(n''-2j-l)}$$

and where the upper limit of the first sum is the smaller of n' or n'' and the upper limits of the second and third sums are either the upper or lower figures depending upon whether $n-k$ is even or odd. In order to visualize these terms and to use them in the numerical calculations the smallest ones are given in Table I. The value of the integral for (n'', n') can be obtained from

TABLE I.

n'	n''	Value of the integral (11)
0	0	1
0	1	$(1/2^{1/2})e_1$
0	2	$(1/2^{1/2})[e_2+c_2]$
1	1	$(1/2)[d_1e_1+a_2]$
0	3	$(3^{1/2}/2)[e_3+c_2e_1]$
1	2	$(1/2)[d_1e_2+c_2d_1+a_2e_1]$
0	4	$(3/2)^{1/2}[e_4+c_2e_2+c_4]$
1	3	$(3/8)^{1/2}[d_1e_3+c_2d_1e_1+a_2e_2+a_2c_2]$
2	2	$(1/2)[d_2e_2+c_2d_2+b_2e_2+b_2c_2+a_2d_1e_1+a_4]$
0	5	$(15^{1/2}/2)[e_5+c_2c_3+c_4e_1]$
1	4	$(3^{1/2}/2)[d_1e_4+c_2d_1e_2+c_4d_1+a_2e_3+a_2c_2e_1]$
2	3	$(3/8)^{1/2}[d_2e_3+c_2d_2e_1+b_2e_3+b_2c_2e_1+a_2d_1e_2+a_2c_2d_1+a_4e_1]$
1	5	$(15/8)^{1/2}[d_1e_5+c_2d_1e_3+c_4d_1e_1+a_2e_4+a_2c_2e_2+a_2c_4]$
2	4	$(3^{1/2}/2)[d_2e_4+c_2d_2e_2+c_4d_2+b_2e_4+b_2c_2e_2+b_2c_4+a_2d_1e_3+a_2c_2d_1e_1+a_4e_2+a_4c_2]$
3	3	$(3/4)[d_3e_3+c_2d_3e_1+b_2d_1e_3+b_2c_2d_1e_1+a_2d_2e_2+a_2c_2d_2+a_2b_2e_2+a_2b_2c_2+a_4d_1e_1+a_6]$
2	5	$(15/8)^{1/2}[d_2e_5+c_2d_2e_3+c_4d_2e_1+b_2e_5+b_2c_2e_3+b_2c_4e_1+a_2d_1e_4+a_2c_2d_1e_2+a_2c_4d_1+a_4e_3$ $+a_4c_2e_1]$
3	4	$(3/8^{1/2})[d_3e_4+c_2d_3e_2+c_4d_3+b_2d_1e_4+b_2c_2d_1e_2+b_2c_4d_1+a_2d_2e_3+a_2c_2d_2e_1+a_2b_2e_3$ $+a_2b_2c_2e_1+a_4d_1e_2+a_4c_2d_1+a_6e_1]$
4	4	$(3/2)[d_4e_4+c_2d_4e_2+b_2d_2e_4+b_2c_2d_2e_2+b_4e_4+c_4d_4+b_4c_4+a_2d_3e_3+a_2b_2d_1e_3+$ $+a_2c_2d_3e_1+a_2c_2b_2d_1e_1+a_4d_2e_2+a_4c_2d_2+a_4b_2e_2+a_4b_2c_2+a_6d_1e_1+a_8]$

$(n'n'')$ by interchanging subscripts on "b" and "c" and on "d" and "e", i.e $a_2b_2c_0d_1e_2$ becomes $a_2b_0c_2d_2e_1$. All coefficients with the subscript zero are equal to unity and are therefore omitted.

III. COMPARISON WITH EXPERIMENT

In the preceding section a formula is developed which allows the matrix elements of the electric moment to be calculated for vibration transitions in symmetrical diatomic molecules. The relative intensities of the bands in the electronic-vibration spectra of these molecules are calculated by squaring the integral (11) and multiplying by the fourth power of the frequency and by the distribution factor of molecules in the initial state.[9] It is somewhat difficult to know exactly what frequency to multiply by because the intensity obtained should apply to the sum of all the rotational transitions which have the same vibrational and electronic quantum numbers. If the rotational quantum number in Eq. (4) is set equal to zero then we should expect our calculated intensities to agree with those in the $Q(0)$ branch corresponding to the given electronic and vibrational transition. However, in any case, the changes in the frequencies associated with different vibrational transitions are very small since the change in vibrational energy is very small compared to the change in the electronic energy. Since the frequency factors do not appreciably affect the comparison of the calculated results with experiment, they have been omitted in the tables given below.

It is practically impossible at present to calculate accurately the expected intensity in emission spectra because the distribution factor for the initial state depends not only upon the temperature but also upon the method of excitation and upon whether or not the molecules have reached their initial excited levels by means of a transition from a higher level. It should be possible however, to calculate the relative intensities of those bands which originate from the same initial vibrational level and the emission diagrams should show agreement in the horizontal rows. In absorption spectra it is easily possible to calculate the expected absorption intensity for a given temperature because in this case the distribution factor is merely the appropriate Boltzmann factor. However, when we try to compare the calculated results with experiment we find that the exact temperature or pressure is seldom recorded in absorption spectrum intensity measurements. In the following calculated results no attempt has been made to include the temperature factor because of the uncertainty in the exact temperatures used in obtaining the experimental results. We have calculated the intensities for the first few vibrational levels only (because of the restriction to harmonic oscillations) so that in some cases the temperature distribution will not vary greatly from a uniform distribution and merely the squares of the integral (11) should be in approximate agreement with the experimental results, in other cases, only the agreement in the columns (for absorption) should be considered.

In making the theoretical intensity calculations the values of α and δ are first calculated. The value of α which is given by $(\nu_0''/\nu_0')^{1/2}$ is usually very well known since it comes from an analysis of the vibrational energy levels themselves. The value of α may therefore be determined to within three significant figures. The value of δ depends upon the values of the separations of the nuclei which in turn depend upon the values of the moments of inertia given by the analysis of the rotational spectrum. The values of the nuclear separations thus calculated are usually accurate only to within about 1 percent so that δ which depends upon the difference in the separations in the initial and final states ($\delta=0.1221\ (r_0'-r_0'')\ (\nu_0''M)^{1/2}$) is, in general, susceptible to quite large errors. The next step in the calculations

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[9] Cf. A. Sommerfeld, Ergänzungband, p. 96.

is to evaluate the coefficients a, b, c, d, and e given after Eq. (11). The triple sum in Eq. (11) is then evaluated which in the highest state ($n'=4$, $n''=3$) considered, consists of 13 terms. In the diagrams given below the observed and calculated intensities are given in the usual double-entry form. In every case the observed intensities are placed on top and the corresponding calculated ones are given directly underneath them. Each element will be treated in a separate section.

a. Sodium.

The experimental and calculated data for the green absorption band of sodium (Na_2) are shown completely in Fig. 1. It may be seen that here the agreement is rather remarkable, perhaps much better than one would expect with the available intensity measurements which are only estimates.[10] The experimental intensities are taken from Fredrickson and Watson.[11] The values of the frequencies and of the nuclear separations are taken from Loomis and Wood[12] and give for α and δ the values 1.130 and 2.43 respectively. Fredrickson and Watson give the nonappearance of the bands (1–2), (2–1), (3–1), (2–2) and (1–3) as an especial characteristic of this system and the calculated intensities indicate very definitely the fact that these particular bands should be very faint. The calculated intensities in the positions (1–2) and (2–1) are quite sensitive to changes in the nuclear separations and indeed, when the writer first calculated these intensities, he used the value $r_0' - r_0'' = 0.40 \cdot 10^{-8}$ cm given by Fredrickson and Watson and found complete disagreement with experiment since the values in the positions (1–2) and (2–1) were approximately 12 on the same scale as used in Fig. 1. Later he found that Loomis

n'' n'	0	1	2	3	4
0	2 2.00	5 4.52	5 4.78	5 5.32	4 3.98
1	9 5.82	6 5.00	— 1.22	— 0.04	4 1.32
2	8 7.78	— 0.68	— 1.22	3 3.26	— 1.70
3	6 6.28	— 1.02	3 3.26	2 0.40	— 2.38
4	5 3.42	2 4.82	3 0.60	— 1.53	

Fig. 1. Observed and calculated intensities in the green Na_2 absorption band. The observed values are placed on top.

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[10] The Physical Review Referee has kindly pointed out that since at 1000°K the relative distribution in the initial states $n''=0,1,2,3,4$ is 1.00, 0.80, 0.64, 0.51, 0.41 respectively, the agreement in the top row of Fig. 1 can only be accidental and that the agreement in the columns only should be noticed.

[11] W. R. Fredrickson and W. W. Watson, Phys. Rev. **30**, 429 (1927).

[12] F. W. Loomis and R. W. Wood, Phys. Rev. **32**, 223 (1928).

and Wood had pointed our errors in Fredrickson and Watson's analysis and that they gave instead the value $r_0'-r_0''=0.33\cdot 10^{-8}$ cm from which the values given were calculated.

b. Potassium.

Fredrickson and Watson[11] give an intensity diagram for the near red potasium absorption band which is very similar to the green band of sodium. However, as was the case with sodium, the nuclear separations which they give ($r_0'-r_0''=0.43\cdot 10^{-8}$ cm) do not give calculated intensities which agree at all with experiment. It is interesting however, that because of the absence of the (1–2) and (2–1) bands and because of the likeness to Na_2 it is possible to estimate the change in the nuclear separation for K_2. The value of δ which is obtained is almost the same as that for Na_2 and since $(\nu_0''M)^{1/2}$ is practically identical in both cases the value of $r_0'-r_0''$ can be estimated to be close to the same value as for sodium ($0.33\cdot 10^{-8}$ cm) although it may possibly be as low as $0.29\cdot 10^{-8}$ cm. The agreement for only the first few terms when $0.33\cdot 10^{-8}$ cm is used is shown in Fig. 2. The principle point in favor of the argument for the change in separations chosen is that the *only* value, which gives a general agreement throughout all terms, is just the value which reduces the (2–1) and (1–2) terms to a very small value.

n'' n'	0	1	2
0	3 3.00	8 7.02	9 8.97
1	10 8.64	5 7.68	— 1.80
2	8 11.55	— 1.13	2 1.86

Fig. 2. Observed and calculated intensities in the near red K_2 absorption band. The observed values are placed on top.

c. Iodine.

The iodine spectrum is characterized by the fact that intense bands correspond to changes of very large quantum numbers. Because of this fact it is obvious that we cannot expect to calculate the exact intensities by the integral (11) which is derived on the assumption of harmonic oscillations. We can however, draw important qualitative conclusions from this formula. If we restrict ourselves to the first column, that is, to all bands which result from a transition from the lowest initial vibrational state, we find that the most important term in the theoretical calculation is the d term which has the same index as the vibrational quantum number of the end state n'. The constants given by Mecke[13] for iodine give $\alpha=1.300$ and $\delta=14.9$. Because of the large value of δ we find it is just the d coefficients which are extremely

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[13] Mecke, Handbuch der Physik XXI, p. 547.

large, in fact d_{14} is about 20,000 times d_0. The values of the coefficients go up rather rapidly to a maximum at d_{14} and then slowly decrease. To calculate the intensities we must square these values of d and multiply by the square of the normalizing coefficient which tends to shift the maximum intensity in the direction of large quantum numbers. It requires therefore no stretch of the imagination to conclude that the first terms will be insignificant with respect to later ones and that observable terms will begin to appear at about $n'=14$ and extend out into the neighborhood of $n'=60$ or more. The appearance of lines in these positions is in agreement with the experimentally observed intensities.

Because of the effect of the Boltzmann distribution factor, there are very few molecules in the higher n'' states so that the absence of transitions starting from the higher n'' levels is explained even though their calculated transition probabilities are large.

d. Hydrogen.

In the absorption spectrum of hydrogen all the transitions have the same initial quantum level ($n''=0$) and we should therefore expect Eq. (11) to give a fairly accurate representation of their intensities. The intensiy constants for the hydrogen absorption spectra are obtained from the molecular constants given by Richardson and Davidson[14] and are $\alpha=1.786$ and $\delta=4.45$ The agreement of the calculated intensities with the absorption data given by Dieke and Hopfield[15] is shown in Fig. 3. The agreement in this case is not good although it will be seen that the theoretical calculations give about the right number of bands at least. No explanation of these discrepancies can be given but it must be realized that the intensities are in the extreme ultra-violet where it is very difficult to make accurate absorption estimates. Because of the similarity of the higher wave functions one would expect the intensities of the higher observed bands to become gradually smaller rather than to break off suddenly as is shown in the figure. It may be possible too that the fact that a harmonic oscillator was assumed will explain the discrepancies in the bands at the right of the figure.

n'	0	1	2	3	4	5	6	7	8	9
I_0	2	6	8	5	4	8	3	6	4	6
I_c	1.0	7.2	22.5	38.5	39.0	20.7	4.2	0.02	1.2	0.19

Fig. 3. Observed (I_0) and calculated (I_c) intensities for the ultra-violet absorption spectrum of the hydrogen molecule. The initial vibrational state of all of these transitions is the same.

Although as was stated earlier, we cannot expect very close agreement between emission spectra and the calculated intensities the emission spectra of the $3^1B \rightarrow 2^1S$ band system of hydrogen shows some interesting points. The notation and constants are taken from Richardson and Davidson[14] and we find $\alpha=0.784$ and $\delta=-1.008$. The experimental values are taken from

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[14] A. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A125**. 35 (1929).

[15] G. H. Dieke and J. J. Hopfield, Phys. Rev. **30**, 400 (1927).

Kapucinsky and Eymers'[16] intensity measurements. These measurements are in the visible region and were carefully made by means of a registering microphotometer so that great faith may be had in the results. The experimental and calculated intensities are shown together in Fig. 4. It will be seen in this figure that good agreement is obtained except at the positions in which n changes by ±1 units. At these positions the intensities are apparently reversed, that is, the one corresponding to a change in n of $+1$ agrees better in every case with the experimental intensity corresponding to a change of -1 in n and vice versa. No explanation of this fact can be given at the present time.

n \ n''	0	1	2	3
0	286 286	95 223	29 41.8	9.1 1.4
1 2	375 137	35.4 42.6	159 257	56 26.9
2	75.2 73.5	395 72.4	5.4 6.6	61 194
3	(8) 32.6	102 88.4	142 10.9	29.3 24.6

Fig. 4. Observed and calculated intensities in the $3'B \rightarrow 2'S$ emission band system of hydrogen. The observed intensities are placed on top.

IV. Conclusion

On the basis of wave mechanics the intensity of a spectral line is measured by the integral of the product of the electric moment and the wave functions of the initial and of the final states. It is possible to carry this integration through approximately for vibration electronic transitions in symmetrical diatomic molecules. In this way a formula is developed for the intensity of any band in the electronic vibration spectra of these molecules. The intensities of certain spectral bands of Na_2, K_2, I_2, and H_2 are calculated and in some cases rather good agreement with experiment is obtained. It should be noticed that although there are discrepancies in many of the results the general intensity values and the number of lines to be expected agree well with experiment in all cases in spite of the fact that the important constant (depending upon nuclear separations) varies from -1.01 in the $3'B-2'S$ band of hydrogen to $+14.9$ in the absorption spectrum of iodine.

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[16] W. Kapucinsky and J. G. Eymers, Proc. Roy. Soc. **A122,** 58 (1929).