A THEORY OF INTENSITY DISTRIBUTION IN BAND SYSTEMS*

By Edward Condon

Abstract

A theory of the relative intensity of the various bands in a system of electronic bands is developed by an extension of an idea used by Franck in discussing the dissociation of molecules by light absorption. The theory predicts the existence of two especially favored values of the change in the vibrational quantum numbers, in accord with the empirical facts as discussed by Birge.

A means of calculating the intensity distribution from the known constants of the molecule is presented and shown to be in semi-quantitative agreement with the facts in the case of the following band systems: SiN, AlO, CO (fourth positive group of carbon), I_2 (absorption), O_2 (Schumann-Runge system), CN (violet system), CO (first negative group of carbon), N_2 (second positive group of nitrogen), and N_2 (first negative group of nitrogen).

In the case of I_2 there is a discrepancy, if Loomis' assignment of n'' values is used, which does not appear if Mecke's original assignment is used. It is suggested that at least some of the lower levels postulated by Mecke are real but that absorption from them always results in dissociation of the molecule and so they are not represented in the quantized absorption spectrum.

1. Introduction

THE problem of the explanation of relative or absolute intensities of spectral lines stands out today as one of the most important in the whole field of spectroscopy. As yet the problem has hardly received the necessary attention from experimental workers to make attempts at quantitative theoretical treatment profitable. The experimental difficulties of constructing controllable sources of excited materials seem to be yielding but slowly to the tremendous efforts toward their removal which are now being made. However, as is known, considerable progress has already been made in the discussion of relative intensities in the fine structure of lines (notably hydrogen Balmer lines in the Stark effect) and more recently in the relative intensities in multiplets in line spectra and of the various lines in the fine structure of individual bands.[1]

When the fine structure of lines or bands is under discussion the experimental problem is considerably easier, for in this case the difficulties of the unknown variation of photographic sensitivity with wave-

---

[1] Sommerfeld, Atombau und Spektrallinien. 4th ed. Chap. 5.

length do not make themselves felt appreciably. But when relative intensities are desired over long stretches of the spectrum, as between the members of a series of lines in atomic spectra or as in a system of bands in molecular spectra, the difficulties of photometric work present themselves in their full force. The result is that today there are few quantitative data in this field. In the case of the individual bands of a system,—the special subject of this article,—one has only the rough visual estimates of the observers; sometimes nothing better than a knowledge of the presence or absence of the band in question under very roughly described conditions of excitation and observation.

It seems worth while, however, to undertake an attempt at a theoretical correlation of the outstanding characteristics of the observed data with the quantum theory model for the emitter of the band spectra of diatomic molecules. The theory presented here is one of the relative likelihood of the various possible changes in the vibrational quantum number and makes no attempt to explain the distribution of molecules in the initial state. The distribution in the initial state, in cases approaching thermal equilibrium, should be governed by the Maxwell-Boltzmann distribution law. This is apparently the case *within the accuracy of the known data* for absorption spectra, where deviations from thermal equilibrium are least important.[2] The Maxwell-Boltzmann law seems also to hold remarkably well in some cases of violent electrical excitation in discharge tubes where one hardly expects to find thermal equilibrium. Perhaps this is a reflection of the fact that the Maxwell-Boltzmann law is one of a sort of maximum chaos, and it matters not whether the chaos results from disordered heat motions or irregular electrical conditions. To be more concrete, if n' is the vibration quantum number of the excited electronic state of the molecule and n'' that of the normal state of the molecule, then the theory presented here undertakes the discussion of what Birge has called an n' progression for the emission process or an n'' progression for the absorption process.

One expects the considerations of which use is made in the model discussed to be of an approximate nature only. They are based on certain kinematic relationships existing between the vibratory motions in the two electronic states concerned. As the simple mode of discussing the model is one which, without quantum theory, would yield fractional changes in the vibrational quantum numbers, the question arises as to the proper modification of the results of the continuous theory in order

to fit the discontinuous quantum theory. There is as yet no known way of treating this problem so the present results are necessarily approximate.

In view of the fact that the latest development in the disentanglement of the quantum enigma is in the direction of the substitution of another kinematics[3] for the description of mechanical systems whose sizes are of the order of Angstrom units it is thought best not to dwell too long on the attempt to formulate this treatment exactly. Rather it is recorded here as giving results in striking and partially satisfactory agreement with the facts although with the expectation that a better treatment must come through the application of the newer kinematics of Heisenberg, Born, and Jordan.

The modern quantum theory interpretation of electronic bands as presented in Sommerfeld's "Atombau"[4] and in the National Research Council Report on Molecular Spectra (in press) is adopted in this paper. The quantization of the motion of a diatomic molecule leads to energy levels associated with each electronic configuration which are specified by a rotational and a vibrational quantum number, m and n respectively, as given by the following formulas:

$$\frac{E}{hc} = A_n = B_n m^2 = D_n m^4 = F_n m^6 = \cdots$$

$$A_n = \omega^0 n(1 - \alpha n + \cdots)$$

$$B_n = B_0 - \alpha n + \cdots$$

$$D_n = D_0 + \cdots$$

All of the expressions are, in fact, infinite series but the terms indicated suffice for the analysis of most band systems. The derivatives of the potential energy curve at its equilibrium point are given in terms of the empirically determined, ω^0, x, B_0, α $\cdots$ by the formulas:[5]

$$V'(r_0) = 0$$

$$V''(r_0) = c^2 (2\pi\omega^0)^2 \mu$$

$$V'''(r_0) = -\frac{6V''(r_0)\pi\sqrt{2B_0\mu c}}{\sqrt{h}}\left(\frac{\alpha\omega^0}{6B_0^2} + 1\right)$$

$$V^{IV}(r_0) = \frac{2}{V''(r_0)}\left[\frac{5}{6}[V'''(r_0)]^2 - 8\frac{x}{ch\omega_0}[V''(r_0)]^3\right]$$

[3] Heisenberg, Zeits. f. Physik 33, 879 (1925); Born and Jordan, Zeits. f. Physik 34, 858 (1925); L. de Broglie, Ann. d. Physique 3, 22 (1925); Schrödinger, Ann. der Physik 79 459 (1926).

[4] Sommerfeld, Atombau, 4th ed., Chap. 9.

[5] The formulas are given by Born and Hückel, Phys. Zeits. 24, 1 (1925). The nomenclature used here is that of the Report on Molecular Spectra.

in which c is the velocity of light and μ is the harmonic mean of the masses of the two atoms in the molecule.

2. General Theory for Abrupt Structural Changes

The theory of transition probability which will now be developed is an outgrowth of a picture proposed by Franck for a mechanism for the dissociation of molecules by absorption of light.[6] Briefly Franck's picture is as follows:

In a "cold" gas the molecules are not vibrating and are in their lowest electronic level so that the nuclear motions are governed by $V_1(r)$. If now a light quantum is absorbed which is of sufficient energy to bring the molecule into an electronic excited state, it is natural to suppose that in thus changing the electronic energy of the molecule no other specific action is exerted by the light on the molecule. The absorption of light merely substitutes a new law of nuclear interaction, say $V_2(r)$ for the old one $V_1(r)$. But since this new one has a different equilibrium position, the atoms, at the instant after the absorption, will be away from equilibrium and so start to vibrate. Should it happen that

$$V_2(r_{01}) > V_{2\max}$$

where $V_{2\ \max}$ is the maximum value of $V_2(r)$ in the range $r_{01} < r < \infty$ then the molecule will tend to execute oscillations of infinite amplitude, i.e., the molecule will dissociate. Thus Franck contemplates the photochemical dissociation of a molecule by a simple absorption of light.

It is natural to extend this point of view to the effect of an electron transition in a molecule either in absorption or emission and whether the molecule be vibrating in the initial state or not. The electron transition is supposed to happen in a negligibly short time as compared to the period of the nuclear vibrations. If the transition occurs at the instant when the separation of the atoms is r and the relative momentum is p_r then one supposes that the transition does not alter the instantaneous values of r and p_r but merely substitutes a new potential energy function, say $V_2(r)$, for the old one, say $V_1(r)$. The values of r and p_r at the instant of transition determine exactly a vibrational motion in the final state.

In general, of course, the vibrational motion so determined is not one of the states allowed by the quantum conditions. It becomes necessary, therefore, to suppose that the vibrational motion of the final state is not strictly governed by this principle but that it merely tends to take up the quantized vibration nearest to the one indicated by this principle.

[6] Franck, Trans. Faraday Society (1925).

Here a certain ambiguity appears which is akin to that which occurs in all other cases where attempts are made to reason accurately from properties of the orbits, other than their energies.

It is easy to give a general analytical formulation of the action governing the vibrational transition. Disregarding rotation and writing p for p_r, and q for r one has for the Hamiltonian functions of the initial and final states:

$$H_1 = \frac{p^2}{2\mu} + V_1(q)$$

$$H_2 = \frac{p^2}{2\mu} + V_2(q)$$

If the motion in either state is solved by the Hamilton-Jacobi method leading to the introduction of the action and angle variables, $J_1 w_1$ for the initial state and $J_2 w_2$ for the final state one finds relations of the form

$$p = p_1(J_1, w_1)$$

for the initial state,

$$q = q_1(J_1, w_1)$$

and similar relations for the final state. On the assumption underlying the work, if the electron transition takes place at an instant when the initial values of J and w are J_1, w_1 then the values of J and w after the transition, i.e., J_2 and w_2 will be given by the equations:

$$p_2(J_2, w_2) = p_1(J_1, w_1)$$

$$q_2(J_2, w_2) = q_1(J_1, w_1)$$

Or solving these equations for J_2 and w_2 one finds that:

$$J_2 = J_2(J_1, w_1)$$

$$w_2 = w_2(J_1, w_1)$$

so that the final motion is wholly determined by the initial motion. By the quantum conditions J_1 equals $n_1 h$ and J_2 equals $n_2 h$ where n_1 and n_2 are integers. It is thus seen that the solution for J_2 will not, in general, give an integral value. The phase of the final motion as given by w_2 plays no rôle in the spectroscopic theory. Moreover w_1 enters through a function which is periodic, with period 1 with respect to this variable. Thus the full range of possible values of J_2 corresponding to any J_1 is obtained by letting w_1 range from 0 to 1. From the general dynamical theory w_1 increases linearly with the time. Failing any other indications on this point, one may say that the electron transition is just as likely

to occur at one instant as at another, and thus there is a definite probability assigned to each range of J_2 to J_2+dJ_2.

It is clear that if all values of w_1 are equally probable then the values of J_2 corresponding to the small values of dJ_2/dw_1 will be strongly weighted. But $dJ_2/dw_1=0$ give the maxima and minima of the possible transitions so that these extremes are to be regarded as more probable than the other allowed jumps.

But the uncertainty of how to treat the fractional n_2 and the inaccuracy of the experimental data make it fruitless to attempt to consider such detailed questions as the accurate relative probabilities of the transitions. For a given J_1 there will be a maximum and minimum value of J_2 given by the theory. Moreover the most probable transitions, it will appear later, are to the extremes of J_2 if the times of electron transition be taken as equally probable. Therefore in discussing the relationship of the theory to empirical facts, only the extremes of J_2 for each J_1 have been computed.

Looking over the theory as just developed, it is to be emphasized that at least the extrema of J_2 for each J_1 are governed entirely by the energy functions $V_1(r)$ and $V_2(r)$. These in turn, as has been pointed out, are fixed by the positions of the bands in the spectrum. Thus there are no adjustable constants appearing in the theory so that *the vibrational transition probabilities are sharply correlated with the structure of the band system as regards position in the spectrum.*

The actual solution of the equations which present themselves in the case of the non-harmonic oscillator is prohibitively lengthy. In the following section the explicit formulas are developed for the case in which all derivatives of $V_2(r)$ and $V_1(r)$, higher than the second, vanish (harmonic oscillator). A graphical mode of treating the non-harmonic case is also presented.

3. Explicit Formulas for the Harmonic Oscillator

In the case in which $V_1(r)$ and $V_2(r)$ are parabolic the modes of vibration are simple harmonic in both initial and final states and the explicit development of the formulas is quite simple. Thus let us assume:

$$V_1(q) = \tfrac{1}{2}K_1(q-q_{01})^2$$
$$V_2(q) = \tfrac{1}{2}K_2(q-q_{02})^2$$

The solution for p and q in terms of J and w for the harmonic oscillator is well-known.[7] One has for the final state:

[7] Born, Vorlesungen über Atommechanik, pp. 39, 57.

$$p_2(J_2, w_2) = \sqrt{2\mu\nu_2 J_2}\cos 2\pi w_2$$

$$q_2(J_2, w_2) = q_{02} + \frac{1}{2\pi}\sqrt{\frac{2J_2}{\mu\nu_2}}\sin 2\pi w_2$$

in which the frequency ν_2 is related to the mass μ and the spring constant K_2 by

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{K_2}{\mu}}$$

Similarly for the initial state:

$$p_1(J_1 w_1) = \sqrt{2\mu\nu_1 J_1}\cos 2\pi w_1$$

$$q_1(J_1 w_1) = q_{01} + \frac{1}{2\pi}\sqrt{\frac{2J_1}{\mu\nu_1}}\sin 2\pi w_1$$

Equating the values of p and q at the instant of the electron transition and writing d for $q_{01} - q_{02}$:

$$\sqrt{2\mu\nu_2 J_2}\cos 2\pi w_2 = \sqrt{2\mu\nu_1 J_1}\cos 2\pi w_1$$

$$\frac{1}{2\pi}\sqrt{\frac{2J_2}{\mu\nu_2}}\sin 2\pi w_2 = d + \frac{1}{2\pi}\sqrt{\frac{2J_1}{\mu\nu_1}}\sin 2\pi w_1$$

Solving for J_2 in terms of J_1 and w_1 by elimination of w_2:

$$J_2 = 2\pi^2\mu\nu_2 d^2 + \frac{1}{2}\left(\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1}\right)J_1 + 2d\sqrt{2\pi^2\mu\nu_2\frac{\nu_2}{\nu_1}}\sin 2\pi w_1 \cdot \sqrt{J_1}$$

$$+ \frac{1}{2}\left(\frac{\nu_1}{\nu_2} - \frac{\nu_2}{\nu_1}\right)\cos 4\pi w_1 \cdot J_1$$

The solution for w_2 in terms of J_1 and w_1 is readily obtained but it is not needed. Introducing the quantum integers n_1 and n_2 in place of J_1 and J_2:

$$n_2 = \frac{2\pi^2\mu\nu_2}{h}d^2 + \frac{1}{2}\left(\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1}\right)n_1 + 2d\sqrt{\frac{2\pi^2\mu\nu_2}{h}\cdot\frac{\nu_2}{\nu_1}}\sin 2\pi w_1 \cdot \sqrt{n_1}$$

$$+ \frac{1}{2}\left(\frac{\nu_1}{\nu_2} - \frac{\nu_2}{\nu_1}\right)\cos 4\pi w_1 \cdot n_1$$

For brevity this will be written:

$$n_2 = A + Bn_1 + C\sqrt{n_1}\sin\theta + Dn_1\cos 2\theta,$$

defining the coefficients A, B, C, D by comparison with the preceding

equation. The extreme values of n_1 corresponding to any n_2 are found by the roots of $dn_1/d\theta = 0$ in the usual way. If $C/4D\sqrt{n_1}| > 1$

$$n_2 = A + Bn_1 \pm C\sqrt{n_1} \mp Dn_1$$

and if $|C/4D\sqrt{n_1}| < 1$ in addition to these also secondary maxima, given by $n_2 = (A - C^2/8D) \pm C^2/4D + (B+D)n_1$ the $\pm$ sign being taken the same as the sign of $C/4D$.

As has already been remarked, the extreme allowed transitions are the most probable ones and therefore these equations for the extrema give the bands which one expects to be strongest in a band system.
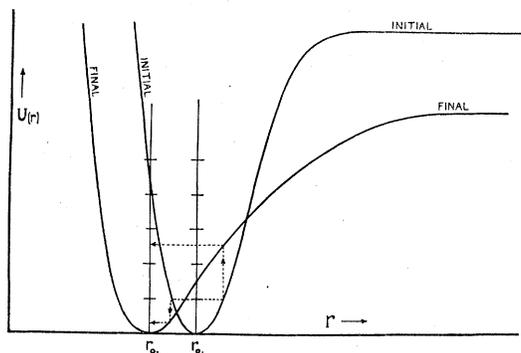

Fig. 1. Typical relation of the potential energy curves, illustrating graphical method of finding favored transitions.

The formulas for the non-harmonic oscillator can be obtained by successive approximations in a purely analytical way but it is easier to resort to an approximate graphical method. $V_1(r)$ and $V_2(r)$ are supposed to have been determined, in the neighborhood of r_{01} and r_{02} respectively from the analysis of the energy levels of the band system. Suppose these plotted on the same piece of paper. Also suppose the vibrational energy levels marked off as in Fig. 1. Then when the molecule vibrates in either electronic state with a known number of quanta it is easy to see what the amplitude of the motion is, for from the energy integral, $p = 0$ when

$$V(r) = W$$

if W is the energy of the vibratory motion. It is at the two extreme positions that the vibrator spends most of the time, i.e., the electronic transition is most likely to occur when the vibrator is in one of these

extreme positions. At these extreme values of r for a vibratory motion given by $V_2(r)$, if $V_1(r)$ is suddenly made the law governing the motion then one sees directly from the figure what will be the amplitude and hence the energy of the new motion. Thus two most probable transitions are determined for each value of the quantum number in the initial state.

This graphical method, as will appear later, indicates how very sensitive the theory is to slight uncertainties in the functions, $V(r)$. In the next section are given the details of the application of the theory to all systems for which the necessary data are available.

4. APPLICATION TO KNOWN SYSTEMS

It will now be seen how far the model employed accounts for the main observed features of intensity distribution in band systems. These have
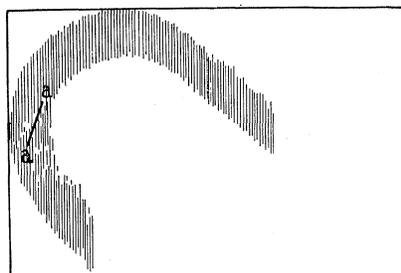

Fig. 2. Typical distribution of intensity in band system
(n' ordinates, downward; n'', abscissas).

been discussed by Birge[8] who points out that it is a general rule that for each value of n' (the quantum number of the initial state for emission) there are two preferred values of $n' - n''$. On a double entry table as normally used, the n' being plotted downward as ordinates and the n'' to the left as abscissas the locus of the strong bands is a parabolic looking curve; i.e., the strong bands form a locus somewhat like the shaded part in Fig. 2. The size of this general locus with regard to the coordinate scale varies greatly from system to system, the branches being coincident for SiN, slightly separated for AlO, widely separated for CO while the scale for iodine is so great that only the part near the origin (a in the figure) is known. In this section the connection between these observed distributions and the theoretical predictions will be examined.

[8] Birge, Phys. Rev. **25**, 240 (1925), Abstract No. 23, also Chap. IV, Sec. 4, Report on molecular spectra.

The band systems to be treated are in order, SiN, silicon nitride; AlO, aluminum oxide; CO, 4th positive group of carbon; I_2, iodine; also O_2, Schumann-Runge system, CN, violet cyanogen; CO^+, first negative group of carbon, N_2, second positive group of nitrogen and N_2^+, first negative group of nitrogen. Of these nine systems, the first four are typical of the increasing scale of the intensity distribution and are discussed in greater detail. In CO and I_2 the deviations from the harmonic law of force are considerable. For these cases corrections for the deviations are discussed as fully as the data allow. For the remaining five systems the observed intensity data together with the theoretical curve calculated from an assumption of harmonic force law are presented as additional examples of the semi-quantitative correctness of the theory.
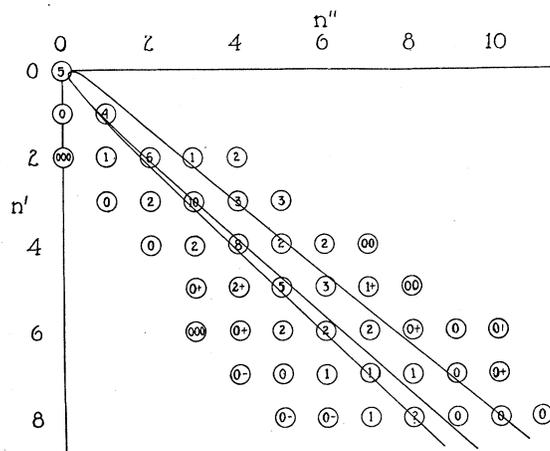

Fig. 3. The band system of silicon nitride.

In Table I are collected together all of the molecular constants which are needed for a discussion of the systems according to the harmonic force law. In every case the figures are taken from a large table of constants in Chapter IV of the National Research Council Report on Molecular Spectra. In the last four columns of the table are given the four constants A, B, C, D which occur in the formula for n'' in terms of n' as computed for the emission process. C.G.S. units are employed. A quantity with ' refers to the initial state and '' to the final state of the emission process. $\omega^{0'}$ is the ν_1 of the previous section expressed in cm^{-1} instead of sec^{-1}, similarly for $\omega^{0''}$ and ν_2.

Turning now to the first system, one has available the estimated intensities by Mulliken.[9] These are plotted in Fig. 3. Here there is but a

[9] Mulliken, Phys. Rev. **26**, 319 (1925); Jevons, Proc. Roy. Soc. **89A**, 187 (1913–14).

Table I.—Summary of molecular constants

Carrier	$\mu \times 10^{24}$	ν_e^* cm^{-1}	$\omega^{0\prime}$ cm^{-1}	$\omega^{0\prime\prime}$ cm^{-1}	$I_0' \times 10^{40}$	$I_0'' \times 10^{40}$	$r_0' \times 10^8$	$r_0'' \times 10^8$	$d \times 10^8$	A	B	C	D	$(C/4D)^2$
SiN	15.417	24234.2	1016.3	1145.0	37.8	37.2	1.567	1.554	+0.013	0.0269	1.007	+0.349	−0.119	0.537
AlO	16.60	20635.3	864.8	970.	46.01	43.38	1.665	1.617	+0.048	0.335	1.007	+1.23	−0.115	7.1
CO	11.317	64721.	1499.28	2147.74	17.3	14.9	1.24	1.17	+0.07	1.075	1.065	+2.485	−0.366	2.88
I₂	104.7	15598.3	126.52	213.76	1210.	787.	3.40	2.74	+0.66	88.0	1.140	+24.4	−0.548	124.
					1115.	720.5	3.622	2.622		82.8		+23.62		
O₂	13.17	49359.3	708.	1565.	34.22	19.2	1.61	1.21	+0.40	29.8	1.331	+16.24	−0.879	21.4
CN	10.67	25799.8	2143.9	2055.64	14.140	14.647	1.151	1.172	−0.021	0.875	1.001	−1.833	+0.043	113.
CO⁺	11.317	45637.7	1704.42	2197.03	15.4	14.05	1.17	1.11	+0.06	0.809	1.033	+2.045	−0.256	3.98
N₂⁺	11.558	29653.1	2018.66	1718.40	15.24	16.98	1.149	1.212	−0.063	0.712	1.013	−1.56	+0.161	5.87
N₂⁺	11.558	25565.9	2396.0	2187.4	13.35	14.41	1.075	1.117	−0.042	0.403	1.004	−1.213	+0.092	10.9

*ν_e gives the frequency of the origin of the 0-0 band.

single ridge of strong bands. The figure shows the curve of most probable values of n'' as a function of n', calculated from the molecular constants according to the theory. As the theoretically double-branched curve is here scarcely an integer in width, it is natural that the double branch should have merged into one for the rough correspondence in question. This molecule is one which shows a doubling of the lower branch due to the cos 2θ term in the formula. The strong bands coincide exactly with this doubled line.

The next typical case is that of aluminum oxide. Here the experimental data both of Birge and also of Eriksson and Hulthén show clearly the double ridge of strong bands.[10] Here the curve computed from the molecular constants for the locus of the strong bands is open enough so that the branches should appear distinct, as in fact they are. The lower branch of the theoretical curve agrees precisely with the data, while the upper branch is slightly high. This distribution of intensity is by far the most common in the systems of bands which have thus far been analyzed on the quantum theory, as can be seen in Table I from inspection of the table of values of A, B, C, and D.

Extending the sequence of increasing scale for the distribution curve, the next example is the great system of the fourth positive group of carbon which is now known to be due to carbon mo-

[10] Birge has made estimates from unpublished spectrograms taken by him at the University of Wisconsin. Also Eriksson and Hulthén, Zeits. f. Physik **34**, 775 (1925).

noxide.[11] In this one system, which extends from about 2650A to 1300A there are known more than 150 different bands. The great extent of this system over the frequency scale (40,000 cm^{-1}) naturally furnishes a severe test of any intensity theory. Unfortunately there are here no even semi-quantitative intensity data. In fact no one observer has ever photographed the entire system. Because of its great extent, however, the main features of the distribution are indicated by a diagram which shows simply which bands are observed. This accordingly has been done in Fig. 6. The full line gives the curve of the intensity distribution as computed by the simple theory based on the harmonic law of force.
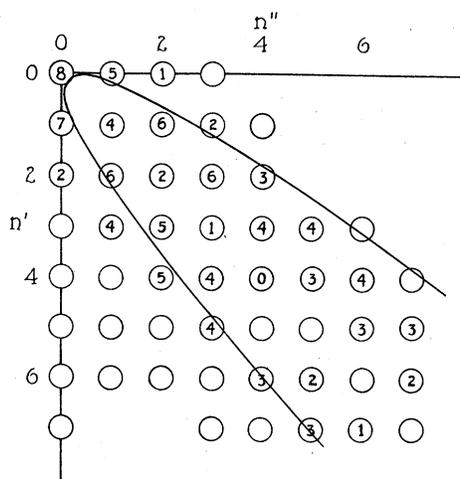
Fig. 4. The band system of AlO.

The analysis of the fine structure of the bands is so incomplete that it is only possible in a rough way to find the corrections due to deviations from the harmonic force law. In fact no fine structure work has been carried out on this system. Data on the initial state may be obtained since this, according to the analysis of Birge, is also the final state of the Angstrom CO bands. The moment of inertia in the final state is obtained from the infra-red CO rotation vibration bands. Besides the data given in Table I, the following figures on the 4th positive group are used in this work:

$$x'\omega^{0\prime} = 17.24 \qquad \alpha' = 0.023$$
$$x''\omega^{0\prime\prime} = 12.703 \qquad \alpha'' = ?$$

By means of the formulas for the coefficients in the law of force already given, it is possible from these data to compute force law curves for both

[11] Birge, Nature **117**, 229 (1926); Lowry, J.O.S.A. **8**, 647 (1924).

states, but with some ambiguity and considerable uncertainty in the final state, for which no α value is known. Writing the expansion for the potential energy in the form

$$V = u_2(r-r_0)^2 + u_3(r-r_0)^3 + u_4(r-r_0)^4 + \cdots$$

in which the unit of energy is spectroscopic wave numbers (cm^{-1}) while $(r-r_0)$ is expressed in Angstrom units one readily finds from the formulas previously given the following expressions for u_2 u_3 and u_4 in terms of the band structure constants:

$$u_2 = \frac{10^{-16}V''(r_0)}{2!hc} = [0.95641-3](\omega^{0^2}\mu)$$

$$u_3 = \frac{10^{-24}V'''(r_0)}{3!hc} = -[0.27924-1]u_2\sqrt{B_0\mu}\left(\frac{\alpha\omega^0}{6B_0^2}+1\right)$$

$$u_4 = \frac{10^{-32}V^{IV}(r_0)}{4!hc} = \frac{1}{u_2}\left(\frac{5}{4}u_3^2 - \frac{8}{3}u_2^3\frac{x}{\omega^0}\right)$$

In these expressions the unit of μ is 10^{-24} gm as in Table I, and the quantities in brackets are the logarithms of the coefficients of the corresponding quantities.

When the formulas are applied to the known data for the initial state in CO one obtains the following values:

$$u_2' = 2.30 \times 10^5$$
$$u_3' = -6.00 \text{ ``}$$
$$u_4' = +8.84 \text{ ``}$$

For the final state a value of α is lacking. In computing the potential energy curve what seems like a reasonable value of α has been used, namely 0.02. This compares well with the known values for systems which have been analyzed. The coefficients found on this assumption are:

$$u_2'' = 4.718 \times 10^5$$
$$u_3'' = -12.59 \text{ ``}$$
$$u_4'' = +25.66 \text{ ``}$$

In Fig. 5 are drawn to scale the potential energy curves of the initial and final states in a form suitable for the application of the graphical method of predicting the intensity distribution. In Fig. 6 is given in the curve marked "corrected law" the theoretical position of the two ridges of intense bands as obtained by this method. It is clear that the corrected law improves the agreement for the lower branch while leaving almost unaltered the good fit of the other branch.

Passing now to the band system of iodine,[12] the largest known band system, it is essential to use the higher terms in the law of force since the change in the moment of inertia between the initial and the final states is very large.

The calculations make use of the following data in addition to that given in the table:

$$\alpha' = 0.00015 \qquad\qquad x' \omega^{01'} = 0.85$$
$$\alpha'' = 0.00011 \qquad\qquad x'' \omega'^{011'} = 0.592$$
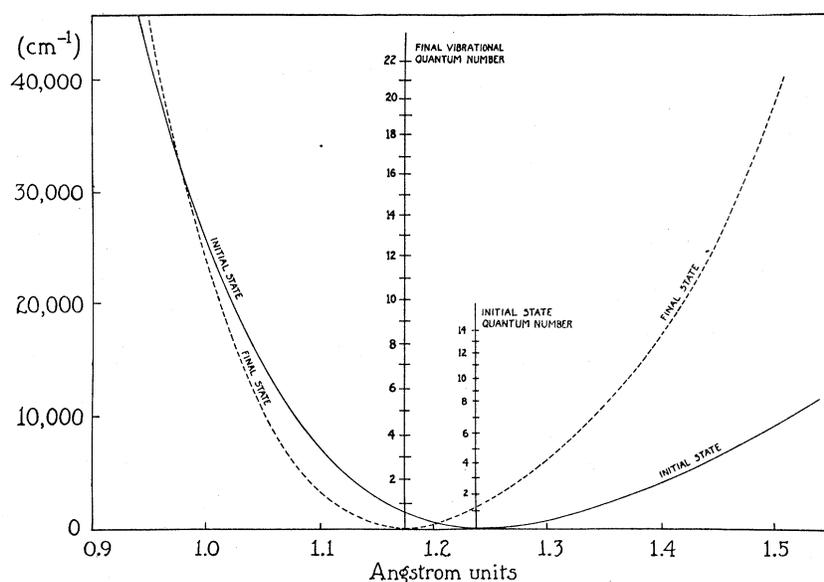
Fig. 5. The potential energy curves for the two electronic states involved in the fourth positive group of carbon (CO).

The resulting values of the coefficients in the potential energy function are:

	Initial	*Final*
u_2:	$+1.537 \times 10^4$	$+4.313 \times 10^4$
u_3:	-2.906 "	-6.002 "
u_4:	$+3.580$ "	$+4.014$ "

[12] The analysis is due to Mecke, Ann. d. Physik **71**, 104 (1923), with Loomis' revision of the quantum assignment. The values of B_0^8 and α are due to Loomis (Chapter VI, Report on Molecular Spectra), that of α'', however, having been previously given by Kratzer and Sudholt, Zeits. f. Physik **33**, 144 (1925). As Loomis points out, the values of α are quite uncertain. For new observations on resonance spectra, see Dymond, Zeits. f. Physik, **34**, 553 (1925).

As in the case of CO, there are no intensity measurements available for this system of bands. The data are due to Mecke and give merely the presence or absence of the various bands. The system is thus plotted in Fig. 7. Here the data are for the *absorption* spectrum rather than for emission as in the examples previously given. To be consistent with the other examples, however, the terms "initial" and "final" in the foregoing set of constants have been chosen so as to refer to the *emission* process. In the absorption process, n'' becomes the initial quantum number and n' the final. Mecke has already commented on the peculiar intensity distribution in I_2, his Fig. 4 contrasting it with the more typical dis-
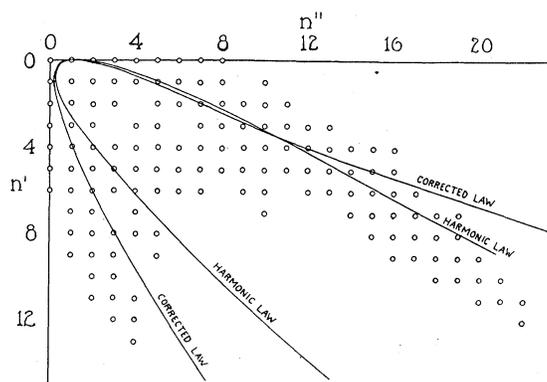

Fig. 6. The observed bands of the fourth positive group of carbon.

tribution of intensity of the violet CN-system. The distribution of intensity is, of course, profoundly modified by the distribution of the molecules among the initial states. This accounts for the great observed decrease in intensity of successive n' progressions, for increasing values of n''.

The curve in Fig. 7 is that which is obtained by the graphical process, using the potential energy curves given by the foregoing set of constants. Here evidently is a wide discrepancy between theory and experiment. The discrepancy may be removed by an alteration in the assignment of vibrational quantum numbers. Mecke's assignment of values of n'' is greater by four than the one, due to Loomis, on which the calculations have been based. Mecke's zero of n'' was chosen to include a place for four anti-Stokes terms in Wood's resonance spectrum. But if the theoretical intensity curve derived from Loomis' assignment is correct it is clear that a molecule in the zero-state initially would favor a transition to an energy state in excess of that required for the dissociation process.

This suggests that when the molecule absorbs light from the unexcited non-vibrating state it is always dissociated and no bands are obtained. It is therefore possible that lower vibrational states exist which contribute, by absorption from them, only to the continuous spectrum of iodine. The existence of such lower states is called for, of course, if there are really the so-called anti-Stokes terms in the resonance spectrum of Iodine. Loomis has, however, given an analysis of the resonance doublets which makes it appear that what were believed to be anti-Stokes terms in the $n'=26$ progression are really due to the excitation of some lines out of other n' progressions. Dymond has recorded observations of
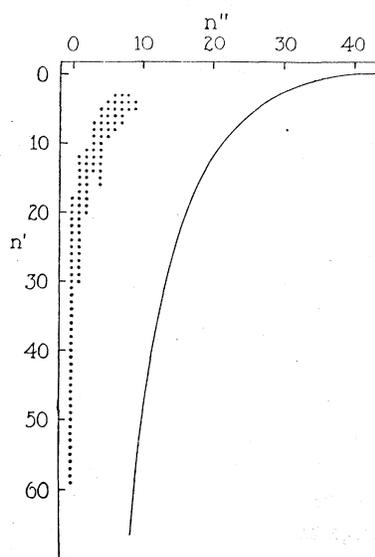
Fig. 7. The absorption bands of iodine (I_2).

anti-Stokes terms in resonance spectra excited by other lines than the green mercury line. It remains to be seen whether Loomis' analysis can be applied to them. It is clear that, since the theory here presented gives the same favored Δn values for absorption as for emission, transitions involving the lower levels in the unexcited state would not appear in the fluorescent spectrum for the same reason that they are not involved in the fully quantized absorption spectrum. Thus it is to be expected that anti-Stokes terms will not appear even though the necessary levels may exist in the molecule.

It is easy to see that a rather small change in the assignment of quantum numbers will make the theory agree with experiment. Full calculations were carried out for the case in which the n'' values were increased

by 5 and the n' by 30. It was found that the discrepancy was about the same but in the other direction. Therefore a good fit could be obtained by some reassignment which makes smaller changes in n' and n''. It seems, however, that agreement on the intensities calls for reassignment of *both* n' and n'', since calculations show that good fits are not obtained if n' alone is altered. Iodine, then, may be tentatively regarded as in agreement with the theory.*

This completes the consideration of the four main sizes of the typical intensity distribution. Of the remaining five, the Schumann-Runge system of oxygen is much like that of iodine in that an unusually large change in the moment of inertia occurs during the electron transition. The other four are medium sized systems like that of AlO.
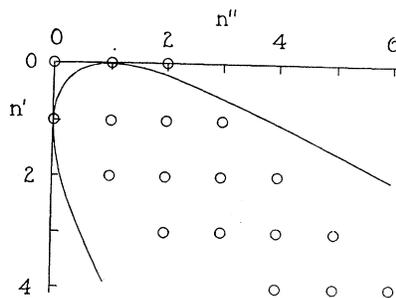

Fig. 8. The violet cyanogen system (CN).

The Schumann-Runge bands of oxygen are quite incompletely known.[13] This name is here given to the system whose $n'' = 0$ progression is known in absorption by the researches of Schumann and others and whose $n' = 0$ progression was photographed in emission by Runge. The recognition of the fact that the Runge and Schumann bands are part of one system is due to Mulliken. The data on the absorption bands has recently been extended by the work of Leifson as interpreted by Birge. All that can be said here is that in absorption Leifson's strongest bands run from $n' = 9$ to a limit at $n' = 21$ with continuous spectrum beyond. Similarly the emission bands measured by Runge correspond to large values of Δn, the actual bands being $n' = 0$, $n'' = 11$ to 17. Here is evidently a preference for large values of Δn which is quite in accord with the theory of this paper. The fine structure analysis of the bands thus

[13] Schumann, Smithsonian Contrib. **29**, no. 1413 (1903); Runge, Physica **1**, 254 (1921); Mulliken, Private communication to Professor Birge; Leifson, Astrophys. J. **63**, 73 (1926); Füchtbauer and Holm, Phys. Zeits. **26**, 345 (1925); Report on Molecular Spectra, Chap. IV, Section 7.
* See note on p. 1201.

far permits only the use of parabolic $V(r)$ curves, but these, when computed from the data of Table I show that in absorption the most probable transition is that beyond dissociation. The calculation shows that from the $n'' = 0$ state the molecule in the absorption process tends to take up over 1.2 volts of vibrational energy or 0.4 volts in excess of that needed for dissociation in the excited state for these bands. Similarly the curves indicate for the $n' = 0$ progression of emission bands a large Δn, much larger in fact than that indicated directly by the Runge bands. Here the higher terms in the force law will undoubtedly operate to reduce the theoretical Δn, so that in this system there is as good agreement as can be hoped for in the present state of analysis of the bands.
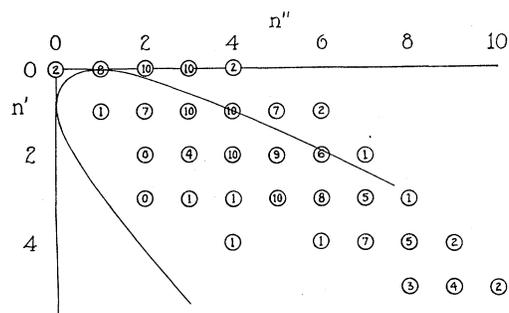
Fig. 9. The first negative group of carbon (CO^+).

The remaining four band systems to be considered present no new features of special interest. They are shown in Figs. 8, 9, 10, 11 in which the intensities are, when given, simply rough visual estimates from the plates. The theoretical curve in each case is based on the formula which assumes simple harmonic oscillators. The data for CN (Fig. 8), are from Heurlinger.[14]

The intensities given for CO^+ (Fig. 9) as well as the molecular constants used are based on the work of Blackburn and Johnson.[15] It is important to note that the theory predicts the existence of some strong emission bands in the far ultraviolet, along the lower branch of the theoretical curve. The single-branched intensity distribution the writer believes is entirely a consequence of the lack of complete experimental data. The intensity estimates for the second positive group of nitrogen (Fig. 10) are due to Birge, being made from inspection of spectrograms taken by E. P. Lewis.[8]

[14] Kayser's Handbuch, v. 5, p. 190.
[15] Johnson, Proc. Roy. Soc. 108A, 343 (1925); Blackburn, Proc. Nat. Acad. 11, 28 (1925).

The data on the first negative group of nitrogen (Fig. 11) are due to Merton and Pilley.[16]

In conclusion it seems permissible to claim that the theory outlined here gives a satisfactory semi-quantitative correlation between the
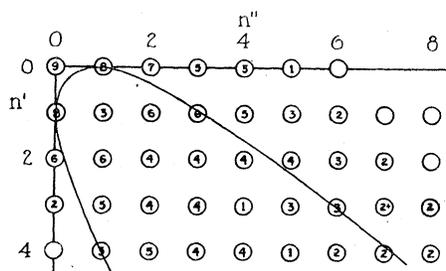

Fig. 10. The second positive group of nitrogen (N_2).

intensity distribution in band systems and the positional structure of the systems by means of a definite mechanical picture of the processes governing transition probabilities. The only previous attempt at a theoretical treatment of this topic is that of Lenz[17] who gave, by application of the correspondence principle to an over-simplified molecular
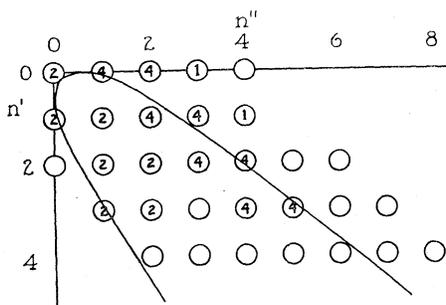

Fig. 11. The first negative group of nitrogen ($N_2{}^+$).

model, some general formulas which, however, were incapable of numerical application to specific cases. On the other hand, Lenz' theory does lead to an understanding of the many and seemingly irregular alternations of intensity in the $n' = 26$ progression of the iodine emission spec-

[16] Merton and Pilley, Phil. Mag. 50, 195 (1925).
[17] Lenz, Zeits. f. Phys. 25, 299 (1924).

trum (Wood's resonance spectrum). This is a thing which is wholly unclear in terms of the theory given here.

It is a pleasure to acknowledge my indebtedness to Professor R. T. Birge who has generously given me the benefit of his knowledge of band spectra and their quantum interpretation. It is also appropriate again to call attention to the fact that my work is merely an extension of a leading thought on this subject by Professor J. Franck.

UNIVERSITY OF CALIFORNIA,
    DEPARTMENT OF PHYSICS,
        July 27, 1926.

Note added to proof.—Since this was written I have learned of the experiments of H. Kuhn (Zeits. f. Physik **39**, 77 (1926)) which seem to show conclusively that the long series of absorption bands which have a convergence limit really do come from the lowest vibration level so that the values of n'' cannot be altered as suggested on page 1198.

GÖTTINGEN,
    November 8, 1926.