MARCH, 1927 *PHYSICAL REVIEW* *VOLUME 29*

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES

III. INTENSITY RELATIONS

BY ROBERT S. MULLIKEN

ABSTRACT

The correspondence principle predicts definite intensity relations for P, Q and R band lines in molecules having a rotational energy term $F(j)=B(j^2-\sigma^2)+\ldots$, provided σ is an electronic quantum number correlated with a precession about the internuclear axis (along which the angular momentum $\sigma h/2\pi$ is directed). Hönl and London have used the summation rule method to obtain exact equations for each of three possible cases $\Delta\sigma=0, \pm 1$; these equations are recast here in more convenient form. According to recent work of Dennison, these equations very probably remain valid in the new quantum mechanics. Theoretical curves for the cases $\Delta\sigma=+1$ and -1 are given.

Various electronic emission bands have been interpreted by the writer as corresponding to electronic transitions $^1S\rightarrow{}^1S$(CuH type), $^1P\rightarrow{}^1S$(AlH, He_2 "series" bands), $^1D\rightarrow{}^1P$ (He_2 λ5733), $^1S\rightarrow{}^1P$(He_2 λ4546, λ6400, and CO Ångstrom bands), with $\sigma=0$ for ^1S, $\sigma=1$ for ^1P, and $\sigma=2$ for ^1D states. Comparison of the predictions of the above theory with the available intensity data on the bands mentioned, assuming in each case thermal equilibrium at a suitable (arbitrarily chosen) temperature, gives in every case qualitative agreement with the predicted distribution for that particular case; usually the agreement appears to be complete within the often comparatively large uncertainties of the data. Oscillation-rotation absorption bands corresponding to $\sigma'=\sigma''=0$ fall under the theory as a special case, and the data on these bands (in particular the quantitative data of Kemble and Bourgin on HCl) agree with the theory. Intensity relations in $^2S\rightarrow{}^2S$ (violet CN type) and $^2P\rightarrow{}^2S$ (ZnH type) transitions are briefly discussed; the intensity relations resemble those for $^1S\rightarrow{}^1S$ and $^1P\rightarrow{}^1S$ transitions, but no satisfactory theory is as yet available.

The close agreement between theory and experiment for spectra interpreted as due to transitions involving ^1S, ^1P, or ^1D states seems to make conclusive the already strong evidence for these interpretations. Furthermore (in connection with the observed selection $\Delta\sigma=0, \pm 1$) it shows that ^1S, ^1P, and ^1D molecular states all belong to a class in which σ is an electronic quantum number correlated with a precession about the internuclear axis.

In $^1S\rightarrow{}^1P$, $^1P\rightarrow{}^1S$, and $^1D\rightarrow{}^1P$ transitions, there exist in practice (cf. II of this series) two rotational states (A and B) for each value of j. The agreements noted were obtained by disregarding the subdivision into A and B sub-states; the fact that agreement was obtained in this way shows incidentally that the a priori probabilities of A and B sub-states must be equal.

Another phenomenon not contemplated by the theory, but present in all the He_2 bands, is that alternate lines are missing in each branch. The cause of this is obscure, but the evidence for its existence is conclusive and so justifies the procedure, which is necessary to obtain the agreement described above between theory and experiment, of inserting in Eqs. (5)–(6) a factor zero for alternate lines in each branch.

INTRODUCTION

THE importance of a study of intensity relations among band lines has been emphasized by Kratzer[1] and by Kemble[2,3]. Up to the present, however, practically nothing has been done to compare experiment with theory except in the case of bands composed of P and R branches only.

As a result of a study of evidence from missing lines, presence of Q branches, and systematic relations for odd and even molecules, the writer has recently concluded[4,5,6,7] that many known band spectra involve rotational terms of the form $B(j^2-\sigma^2)+\cdots$. Band spectra also exist which involve terms of the form $B(j-\rho)^2+\cdots$, while there are others involving more complex forms. A study of observed intensity relations lends strong support, as will be shown in the present paper, to the conclusions just mentioned. For notation, etc., reference should be made to a previous paper.[6]

SURVEY OF WORK ON THE INTENSITY PROBLEM FOR BANDS CONTAINING A SINGLE P AND A SINGLE R BRANCH

Bands without Q branches. Experimentally, known bands consisting of P and R branches and without Q branches comprise (*a*) infrared oscillation-rotation bands with one P and one R branch, such bands ordinarily being observed in absorption (examples: CO and halogen halide bands), (*b*) electronic bands having one P and one R branch (examples, CuH, AgH, AuH, I_2 bands), and (*c*) electronic bands having two P and two R branches, but with the two branches of each kind usually forming a series of close doublets (examples, violet CN and analogous bands).

In the case of oscillation-rotation bands, the presence of a σ is, according to the correspondence principle, a necessary and sufficient condition for the presence of a Q branch;[1,8] the presence or absence of a ρ appears to be immaterial from the standpoint of the correspondence principle. Hence for type (*a*) above, we may conclude that $\sigma=0$, $\rho\geqq 0$. (Throughout this article $\sigma h/2\pi$ and $\rho h/2\pi$ denote components of electronic angular momentum which are respectively parallel and perpendicular to the internuclear axis.) The correspondence principle then gives further information in regard to the expected intensities of the lines of the P and R branches (see below).

[1] A. Kratzer, Naturwiss. **27,** 577 (1923); Ann. d. Physik **71,** 72 (1923).

[2] E. C. Kemble, Proc. Nat. Acad. Sci. **10,** 274 (1924); Phys. Rev. **25,** 1 (1925).

[3] E. C. Kemble, Zeits. f. Physik **35,** 286 (1925).

[4] R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 144 (1926).

[5] R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 151 (1926).

[6] R. S. Mulliken, Phys. Rev. **28,** 481 (1926).

[7] R. S. Mulliken, Phys. Rev. **28,** 1202 (1926).

[8] A. Sommerfeld, Atombau und Spektrallinien, 4th Edition, Chapter 9, (1924).

In the case of electronic bands, the presence of a σ is a sufficient condition for the presence of a Q branch, but not a necessary one[9] unless or until restrictions are placed on the types of electronic motions which are assumed to be possible. The *absence* of a Q branch in types (b) and (c) is, however, satisfactory evidence that σ (i.e. σ' and σ'') is zero; but the correspondence principle gives no definite information in regard to the intensities of the P and R lines unless a molecular model is assumed.

Oscillation-rotation bands without a Q branch. By application of the correspondence principle to bands of type (a), using the device of hypothetical magnetic components to remove degeneracy, Kemble made it probable[2] that the intensities of the lines of both P and R branches should be given by the relation

$$I = ie^{-E_0/kT}, \text{ where } i = a\,\bar{p} \tag{1}$$

Here E_0 is the value of $F(j)$ for the *initial* molecular state, a is to a first approximation a constant (but see below), and $\bar{p}$ is the mean of the a priori probabilities p of the initial and final rotational states. Experimental work of Kemble and Bourgin[10] on the HCl absorption band at 3.46 μ completely confirms Eq. (1), provided $\bar{p}$ is assumed to have the values 2, 4, 6, $\cdots$ for successive lines of each branch, or what is the same thing, provided $p = 1, 3, 5, \cdots$ for the rotational states having $m = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \cdots$.

Fowler[11] and Dieke[13] have shown that Eq. (1) can also be obtained for type (a) bands by a rather formal application of the summation rule, provided the succession of p values 1, 3, 5, $\cdots$ is used, as above; any other choice of p values gives a stepwise-advancing or alternating set of intensities.

Mensing,[14] Fues,[15] and Oppenheimer[16] have shown that for oscillation-

---

[9] H. A. Kramers and W. Pauli, Jr. Zeits. f. Physik **13,** 351 (1923). For further discussion cf. ref. 6, p. 488.

[10] E. C. Kemble and D. G. Bourgin, Nature, June 5, 1926.

[11] R. H. Fowler, Phil. Mag. **49,** 1272 (1925). Fowler attempted to extend the application of the summation rule to the case of bands (including electronic bands) having Q branches. He concluded that the P and R branches (aside from the Boltzmann factor and variability in a) should always be equally intense here, as in bands of the simple $P-R$ type. Kemble then pointed out[3] that this conclusion based on the summation rule is in conflict with the correspondence principle, according to which there are many cases where such equality of P and R branches is not to be expected. Finally, the work of Hönl and London[12] showed that Fowler's conclusion is incorrect, and that the results of the two methods are in harmony.

[12] H. Hönl and F. London, Zeits. f. Physik **33,** 803 (1925).

[13] G H. Dieke, Zeits. f. Physik **33,** 161 (1925).

[14] L. Mensing, Zeits. f. Physik **36,** 814 (1926).

[15] E. Fues, Ann. der Physik **80,** 367 (1926).

[16] J. R. Oppenheimer, Proc. Camb. Phil. Soc. **23,** Part 3, p. 327 (1926).

rotation bands, if $j_e=0$ (i. e. $\rho=\sigma=0$),[17] the new quantum mechanics yields directly the relation $i=a\bar{p}$ of Eq. (1) and the p values 1, 3, 5, $\cdots$.[18]

In a systematic study of known band spectra[6,7] the writer concluded that all known bands of types (a) and (b) are due to transitions in even molecules having $j_e'=j_e''=0$,[17] and $F(j)=Bj^2+\cdots$ with $j=m=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $\cdots$ Such transitions were classified as $^1S\rightarrow{}^1S$ transitions, and it was shown that definite characteristics properties ($j_e=0$, diamagnetic behavior, single rotational states) may be attributed to ^1S states, thus implying that such states correspond to a definite molecular model. It was further concluded that ^1S states belong to a class of states for which $F(j)=Bm^2+\cdots=B(j^2-\sigma^2)+\cdots$, with $\sigma=0$, 1, 2, $\cdots$ for ^1S, ^1P, ^1D, $\cdots$ states, and $j=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $\cdots$ in all (with the condition $j\geqq\sigma$).

With $j=m=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $\cdots$ for ^1S states, the results of the preceding paragraphs require $p=2j$, hence Eq. (1) takes the form

$$I=ie^{-E_0/kT},\ \text{with}\ i=2a\bar{j} \tag{2}$$

If $p=2j$ for ^1S states, it is reasonable to expect the same relation for ^1P, ^1D, $\cdots$ states, and in fact for all electronic states, of both odd and even molecules. According to the writer's conclusions,[4,6] j has integral values for odd molecules but half-integral values for even molecules.[18]

Electronic bands of type (b). The summation rule method of Fowler and Dieke leads to the conclusion that Eq. (1) should hold for electronic bands of type (b) as well as for bands of type (a). The intensity data of Frerichs[20] on the CuH bands, which are of type (b), show that Eq. (1) is indeed applicable here, even to the extent of accounting for the observed superior intensity of the P branch (in emission bands $E_0=E'$ and the exponential factor in Eq. (1) favors the P branch, while in absorption bands $E_0=E''$ and this factor favors the R branch[3,11,13]). The intensity relations in the analogous AgH and AuH bands appear to be of the same type. In the I_2 absorption bands, as Fowler has pointed out,[11] the approximately equal intensity of the two components

---

[17] The assumption made by Kemble, Fowler, and Dieke, that a ρ may be present (other than a "secondary" ρ as discussed in ref. 7, p. 1206), is then probably unnecessary if not unjustified for bands of types (a) and (b).

[18] The new quantum mechanics[14,15,16,27] formulates the rotational energy in terms of a different set of j values than those used here. For the case $j_e=0$, the result is $F(j)=B(j+\frac{1}{2})^2+\cdots$, with $j=0$, 1, 2, $\cdots$, hence $p=2j+1$. Thus it is evident that the j values of the quantum mechanics are analogous to Sommerfeld j values (since $p=2j+1$), while the writer's j values (for which $p=2j$) are analogous to Lande J values. Since the writer has concluded [4,6] that the correct j_e values for molecules are of the Sommerfeld type, it would then be logical to adopt the j values of the quantum mechanics. Largely in order to avoid confusion of notation as compared with earlier papers, the writer's j values will, however, be used here.

[20] R. Frerichs, Zeits. f. Physik **20**, 170 (1923).

in each doublet (one P, one R line) in the "resonance spectrum," again shows the applicability of Eq. (1).

The necessary applicability of Eq. (1) to all bands of type (*b*) is not obvious from the correspondence principle (cf. the discussion in a preceding paragraph); such a definite result would seem to imply a particular molecular model. The solution of this difficulty probably is that precisely the model corresponding to Eq. (1) is required by nature. This idea is supported by the fact that all known bands of type (*b*) appear to be in agreement with Eq. (1). Again, although it is not obvious that restrictions as to model (except that $\sigma=0$ and the absence of a Q branch are assumed) are required in deriving Eq. (1) by the summation rule method, it should be noted that Eq. (1) can be obtained as a special case of a more general Eq. (4) given below which involves definite assumptions in respect to a model. From the evidence presented below in regard to bands where $\sigma\neq 0$, it is altogether probable that the model on which Eq. (4) is based is the correct one for all known bands obeying Eq. (1).

INTENSITY RELATIONS IN BANDS INVOLVING ROTATIONAL TERMS OF THE FORM $B(j^2-\sigma^2)$: APPLICATION OF THE CORRESPONDENCE PRINCIPLE

Application of older form of correspondence principle. In order to apply the correspondence principle to the intensity relations in bands of the type here under consideration, it is necessary to know or to assume something about the nature of the quantity σ (for the cases here considered, $\rho=0$). It will be shown below that predicted and observed intensity relations for a number of band spectra are in agreement if we assume that σ is an *electronic quantum number* which is correlated with a *precession about the internuclear axis.* This assumption is also strongly supported by the fact that in observed bands, according to interpretations recently given by the writer,[6,7] the selection rule $\Delta\sigma=0$ or ± 1 is observed.[21] Furthermore, as Hund has recently shown,[22] precisely such a precession and such a selection rule are to be expected from theoretical considerations. The relation of the results of the present and previous papers of this series to Hund's theory will be discussed in a separate paper.[23]

---

[21] Thus in $^1S\rightarrow{}^1S$ transitions (CuH bands etc.[6]), $\Delta\sigma=0$, while the CO Angstrom, AlH, and He_2 bands furnish examples of $\Delta\sigma=+1$ and $\Delta\sigma=-1$.

[22] F. Hund, Zeits. f. Physik **36**, 657 (1926).

[23] Strictly it is *not* σ itself, but the component σ_k of σ due to orbital electronic angular momentum, with which the precession here under discussion is correlated; σ itself is a resultant of σ_k and σ_s, where σ_s is the component along the internuclear axis of the resultant angular momentum s of electron spin; generally $\Delta\sigma_s=0$ so that $\Delta\sigma_k=\Delta\sigma$. In bands of the ZnH type ($^2P_1\rightarrow{}^2S$, $^2P_2\rightarrow{}^2S$), however, $\Delta\sigma=\frac{1}{2}$ and $1\frac{1}{2}$, but $\Delta\sigma_k=1$, indicating that σ_k is more fundamental than σ, as also follows from Hund's theory. These points will be further discussed in a later paper.

For a precession of the type indicated, the predictions of the correspondence principle for the intensitities of P, Q, and R branch lines are completely analogous to those for the transitions $\Delta j=+1$, 0, and -1 in a line spectrum multiplet. For any selected initial rotational state, if θ represents the angle between j and the figure axis (direction of σ), the intensities should then be given to a fair degree of approximation by the following proportions:[24]

$$\begin{array}{ll} (a) & \sigma'-\sigma''=\pm 1,\ i_P : i_Q : i_R=\tfrac{1}{2}(1\mp\cos\theta)^2 : \sin^2\theta : \tfrac{1}{2}(1\pm\cos\theta)^2 \\ (b) & \sigma'-\sigma''=0,\ i_P : i_Q : i_R=\tfrac{1}{2}\sin^2\theta : \cos^2\theta : \tfrac{1}{2}\sin^2\theta \end{array} \quad (3)$$

In the necessary averaging of the intensity factors of Eq. (3) over the initial and final states, a linear average may be expected to give good results, as in the line spectrum case. Thus suppose $\sigma'=1$, $\sigma''=0$, $j'=2\tfrac{1}{2}$. Noting that $\cos\theta=\sigma/j$, one has $\sigma'/j'=1/2\tfrac{1}{2}$, $\sigma''/j''=0$, and $i_P : i_Q : i_R=\tfrac{1}{2}[(1-1/2\tfrac{1}{2})^2+1] : [1-(1/2\tfrac{1}{2})^2+1] : \tfrac{1}{2}[(1+1/2\tfrac{1}{2})^2+1] =0.68 : 1.84 : 1.48$.

Nature of ^1S *states and relation to* $^1S\rightarrow{}^1S$ *bands.* For the special case $\sigma'=\sigma''=0$, according to Eq. (3*b*), we have $\cos\theta=0$ for all values of j, and $i_Q=0$, $i_P=i_R$. This is in essential agreement with Eqs. (1) and (2).

The applicability of Eq. (2) to all known electronic bands corresponding to $^1S\rightarrow{}^1S$ transitions therefore no longer presents a difficulty but indicates that ^1S molecular states belong to the class of σ-type states, σ being correlated with a precession about the internuclear axis. The fact that ^1S molecular states combine spectroscopically with ^1P states ($\sigma=1$) supports this conclusion, which is furthermore in line with recent theoretical considerations of Hund.[22]

Hönl and London's application of the summation rule. As shown by Hönl and London,[12] Eqs. (3*a*) and (3*b*) can be replaced by more exact equations (Eqs. 4-5-6 below) obtained by an application of the summation rule. Hönl and London's treatment depends on the existance of a close formal analogy between the transitions $\Delta j=0$, ± 1 in line spectrum multiplets and the transitions $\Delta j=0$, ± 1 (Q, R, P, branches) in band spectra, and between $\Delta k=0$, ± 1 in line spectra and $\Delta\sigma=0, \pm 1$ in band spectra, and thus implicitly involves the assumption that σ is correlated with a precession about the internuclear axis as assumed above in connection with Eq. (3).

Hönl and London's equations should of course be applicable to odd as well as to even molecules, using appropriate j values in each case (Hönl and London do not consider this point at any length). The

---

[24] These equations are stated by Hönl and London.[12] The transitions $\Delta\sigma$ (or $\Delta\sigma_k$) $=\pm 1$ or 0 correspond to $\Delta k=\pm 1$ or 0 in the line spectrum case.

equations involve the assumption $p=2j$, which may be expected to hold equally well for odd and even molecules.[25,26]

Eq. (4) is applicable to vibration-rotation as well as to electronic bands; Eq. (2) is now seen to be merely the special case of Eq. (4) corresponding to $\sigma'=\sigma''=0$. Eqs. (5) and (6) are obviously applicable only to electronic bands.

In all cases the relation $I=ie^{-E_0/kT}$ of Eqs. (1) and (2) is applicable, but of course implies thermal equilibrium.

In Eqs. (4)-(6) as given below, Hönl and London's original equations have been considerably altered in form for the sake of convenience in application. In terms of the notation and assignment of j values here adopted, and expressed in terms of $\bar{\jmath}$ (i. e., the mean of j' and j'') rather than of j' or j'' (for Q branches $j'=j''=\bar{\jmath}=j$), the equations are as follows:

For the case $\sigma'=\sigma''=\sigma$,

$$\begin{aligned} i_P=i_R&=2a(\bar{\jmath}^2-\sigma^2)/\bar{\jmath}\\ i_Q&=4aj\sigma^2/(j^2-\tfrac{1}{4}) \end{aligned} \tag{4}$$

For the case $\sigma'-\sigma''=+1$,

$$\left.\begin{aligned} i_P&=a(\bar{\jmath}-\sigma')(\bar{\jmath}-\sigma'+1)/\bar{\jmath}\\ i_Q&=2aj(j-\tfrac{1}{2}+\sigma')(j+\tfrac{1}{2}-\sigma')/(j^2-\tfrac{1}{4})\\ i_R&=a(\bar{\jmath}+\sigma')(\bar{\jmath}+\sigma'-1)/\bar{\jmath} \end{aligned}\right\} \tag{5}$$

For the case $\sigma'-\sigma''=-1$,

$$\left.\begin{aligned} i_P&=a(\bar{\jmath}+\sigma'')(\bar{\jmath}+\sigma''-1)/\bar{\jmath}\\ i_Q&=2aj(j-\tfrac{1}{2}+\sigma'')(j+\tfrac{1}{2}-\sigma'')/(j^2-\tfrac{1}{4})\\ i_R&=a(\bar{\jmath}-\sigma'')(\bar{\jmath}-\sigma''+1)/\bar{\jmath} \end{aligned}\right\} \tag{6}$$

By applying the methods of the matrix mechanics to the closely allied case of the symmetrical rotator, Dennison[27] has obtained equations which are in complete agreement with those of Hönl and London, and there seems no reason to doubt that Eqs. (4)-(6) will remain valid, on the basis of the new quantum mechanics, for the diatomic molecule with $j_e=\sigma$.

---

[25] Hönl and London assume $p=2j+1$ (so that their j values are the same as those of the new quantum mechanics[18]), using, however, the designation m instead of j; they also use m_0 where σ is here used. In the present notation and j numbering, Hönl and London's m would then be replaced by $j-\frac{1}{2}$. However, m as used by Hönl and London is neither m' nor m'' specifically, but represents whichever is the larger of the two ($m=m''=\bar{m}+\frac{1}{2}$ for P, $m=m'=m''=\bar{m}$ for Q, and $m=m'=\bar{m}+\frac{1}{2}$ for R branches). It will then be readily seen that the substitution $m=j$ is correct for both P and R branches, while for Q branches $m=j-\frac{1}{2}$, if the j values are to be those here adopted.

[26] In the analogous atomic case, the relation $p=2j+1$ holds for both even and odd molecules, the j values (Sommerfeld) being integral in the former and half-integral in the latter case.

[27] D. M. Dennison, Phys. Rev. **28**, 329 (1926): Eq. (25). Dennison's m and n correspond to $j_0-\frac{1}{2}$ and σ_0 in the present notation. To get from Dennison's equations to Eqs. (4)–(6), the former must be multiplied by the factor $2j_0$, and also by certain constant factors 1, 2 or 4 (because Dennison's equations are amplitude equations).

Comparison of results of old correspondence principle with those obtained by summation rule method.[11] Since the summation rule method is supposed to involve nothing more than a refinement of the old correspondence principle, Eqs. (3) and (4)-(6) should be in asymptotic agreement for large quantum numbers. That this is the case can readily be verified. The agreement is in fact close even for small quantum numbers if we amplify and somewhat modify Eq. (3) by assuming $i=a\bar{p}=2a\bar{j}$ as in Eqs. (1) and (2), giving to a values proportional to the appropriate trigonometric functions of Eq. (3); Eq. (1) is then in agreement with Eq. (3*b*) for the special case $\sigma=0$. Considering again the case $\sigma'=1$, $\sigma''=0, j'=2\frac{1}{2}$ as an example (cf. above, following Eq.3) one now finds $i_P : i_Q : i_R = 2.04 : 4.60 : 2.96$, whereas Eq. (5) yields the ratio $2 : 5 : 3$.

Inaccuracy of Hönl and London equations for large j values. As shown by Kemble,[2] the factor a in Eq. (1) is not quite the same for the P and R branches in oscillation-rotation bands, and differs more and more as j increases. This difference is due to the variation in the moment of inertia as a result of the vibration of the molecule. The latter renders the rotation non-uniform, and affects the Fourier amplitudes which according to the correspondence principle govern the relative intensities of the P and R branches. This factor always tends to make the P branch more intense, thus assisting the Boltzmann factor in emission bands and opposing it in absorption bands. The effect of this factor remains present on the basis of the summation rule,[28] and in the new quantum mechanics.[16]

The existence of a similar effect in electronic bands seems likely, but the theory has not yet been developed. Other deviations from the relations predicted by Eq. (4)-(6) are to be expected in case of appreciable departure of the electronic angular momentum or its components from rigid orientation with respect to the internuclear axis. The experimental evidence bearing on the above points will be discussed below.

Form of theoretical intensity distribution for specific cases. Effect of Boltzmann factor. According to the preceding discussion, the relative intensities of the lines of a band are determined by the product of a factor i which represents a transition probability *times* an a priori probability $2j_0$, and a factor $e^{-E_0/kT}$, the Boltzmann factor. The factors $2j_0e^{-E_0/kT}$ assume thermal equilibrium for the initial states. This is to be expected in absorption bands, but not in emission bands as ordinarily excited. Nevertheless in practice the rotational energy distribution appears to be normally of a type corresponding well to thermal equilibrium at some specifiable "effective temperature"[29] which

---

[28] R. H. Fowler, Phil. Mag. **50**, 1079 (1925).

[29] The *vibrational* energy distribution does not in general take a form corresponding to thermal equilibrium (cf. R. S. Mulliken, Phys. Rev. **26**, 21–2 and 333 (1925)).

apparently approximates the actual temperature of the surroundings. The question has been examined especially by Birge,[30] in a quantitative study of intensity distribution in the violet cyanogen bands as emitted by various sources.

The types of intensity distribution to be expected for the cases $\Delta\sigma = \pm 1$ are best appreciated by an examination of the theoretical curves in Figs. 1-3 below. For these cases the Q branch is roughly twice as strong as the P or the R branch, while the two latter are roughly equal in intensity. These relations are asymptotically true for large quantum numbers, except for the effect of molecular vibration, and of the Boltzmann factor favoring the P branch. For small values of j, the relative intensities of the branches, especially of the P and R branches, depend markedly on the sign of $\Delta\sigma$ and the magnitude of σ.

It is of interest to note that, as between the P and R branches, the branch which has the larger number of missing lines[6] is always the weaker after it begins. Thus for $\sigma' = 1$, $\sigma'' = 0$, the first P line has $(j' \rightarrow j'') = (1\frac{1}{2} \rightarrow 2\frac{1}{2})$, or $\bar{j} = 2$, while the first R line has $(j' \rightarrow j'') = (1\frac{1}{2} \rightarrow \frac{1}{2})$, or $\bar{j} = 1$; for the P branch the i factors of Eq. (5) have the values 1, 2, 3, . . for $\bar{j} = 2, 3, 4, \ldots$, while for the R branch they are 2, 3, 4, . . . for $\bar{j} = 1, 2, 3, \ldots$ But for $\sigma' = 0$, $\sigma'' = 1$, the first P line has $\bar{j} = 1$ and the first R line $\bar{j} = 2$, and correspondingly the i factors for the two branches are interchanged (cf. Eq. 6) as compared with the previous case. For the case $\Delta\sigma = 0$, where the number of missing lines is the same in the P as in the R branch, the i values likewise are equal for any given value of $\bar{j}$.

The case $\Delta\sigma = 0$ (Eqs. 1 and 4) is illustrated in the present paper only for $\sigma = 0$, where the Q branch vanishes. If $\sigma > 0$, a weak Q branch is to be expected, proportional to σ^2 in intensity (cf. Eq. 4); but in all cases the intensity should fall from the beginning, asymptotically approaching zero, for large j values, as compared with those of the P and R branches.

Relation of Rotational Doubling and Alternating Intensities to the Theory

Rotational doubling. In the development of Eqs. (3)-(6) it was assumed, partly explicitly, partly implicitly, that to each value of j there corresponds just one rotational state, and that P, Q, and R branches all involve the same sets of rotational states. But in practice, as shown in a previous paper,[7] the rotational states are double (A and B sub-states) when $\sigma > 0$, and what is worse, the P and R branches involve $A \rightarrow A$ and $B \rightarrow B$ combinations, while the Q branches involve $A \rightarrow B$ and $B \rightarrow A$ combinations (cf. Fig. 1 and Eqs. 2 and 3 of ref. 7). Hence between Q branches on the one hand and P and R

---

[30] R. T. Birge, Astrophys. J. **55**, 273 (1922).

branches on the other there is an independence which is neither anticipated nor explained by the correspondence principle as applied in the theory outlined above. For example, in a $^1P \rightarrow {}^1S$ electronic transition ($\sigma' = 1$, $\sigma'' = 0$), there is a Q branch involving exclusively initial rotational states of the A type, and a P and an R branch each involving exclusively B-type initial states; the final rotational states are of a single type, probably[7] the B type. Similar anomalies occur in the case of $^1S \rightarrow {}^1P$, $^1D \rightarrow {}^1P$ and other transitions[7] and doubtless in general for combinations of σ-type terms.

If, however, we deliberately overlook these phenomena, by lumping together in all cases the A and B states corresponding to any particular value of j, it is possible to make a comparison between experimental intensity data and the theory as given above. The procedure is justified by the results, as will be shown below, so that it seems permissible to regard the simple theory as an essentially correct first approximation to reality. The success of this method obviously implies an equality of the a factors of Eqs. (5), (6), or (7), for Q as compared with P and R branches, and so indicates equal a priori probabilities for rotational states of the A and B types.

Alternating intensities. Another phenomenon which is not capable of being accounted for by the simple theory is that of alternating intensities in band lines. In this connection reference should be made to a previous paper[7] and to references given there. Formally, alternating intensities of the observed type can be reproduced, so far as is known from the data now available, if in Eqs. (4)-(6),—or other corresponding equations for rotational terms not of the σ type,— the factor a is permitted to have a value or set of values which differ in a constant ratio for alternate lines.[31] The same ratio is applicable to P, Q and R branches, but in such a way that all lines having a common value of j' or j'', rather than of $\bar{j}$, are weakened or intensified. The alternation must therefore be a property of the *molecular states* involved, not of the transition probabilities. This is shown especially by the He_2 bands[7] and the N_2^+ bands.

If, as in the He_2 bands, alternate lines are completely missing in each branch, the intensities of the remaining lines can be plotted against j on a single curve which should be of the same form as if every line were present, if the above-suggested assumption of a constant ratio factor (here zero) is correct. On this basis, as will be shown below, the theoretical and observed intensity curves are in fact in agreement.

As shown in a previous paper,[7] the system of alternate missing levels in the He_2 molecule is such as to render impossible $^1S \rightarrow {}^1S$ and $^1P \rightarrow {}^1P$ transitions. This is a rather extreme example of the difficulties which

---

[31] Cf. also fuller discussion by J. H. Van Vleck, Phys. Rev. **28**, 980 (1926).

the phenomenon of alternating intensities presents, from the correspondence principle standpoint.

COMPARISON OF THEORY WITH EXPERIMENTAL EVIDENCE: BANDS INVOLVING SINGLET ELECTRONIC STATES

Singlet electronic states (^1S, ^1P, ^1D, . . . , with $\sigma=0$, 1, 2, . . .) are characteristic of even molecules. For these molecules the j values are half-integral.

Nature of available data. Comparatively little work has been done on the quantitative measurement of the intensities of band lines. Nevertheless there is a considerable mass of useful data, for the most part of two types (1) eye estimates of photographic blackening (2) measurements or curves of photographic density against wave-length. In the absence of disturbing factors (serious variations of plate sensitivity, etc. with wave-length; effects of impurities; unresolved doublets; lack of care to use a uniform scale in the case of eye estimates; etc., etc.), both these types of data, especially the second, are valuable in giving correctly the *order of intensity* of the lines in a band.

The value of such imformation can be seen from the following considerations. Suppose all the lines of a band (including lines on both the ascending and descending parts of the intensity curves) are arranged in order of intensity (*a*) according to theory (*b*) according to experimental data of the type mentioned. A little consideration will show that substantial agreement of the two modes of arrangement would constitute a verification of the theory falling not far short of being completely satisfactory, a chance agreement being exceedingly improbable.

With data of the type mentioned, the theoretical curves of absolute intensities and the experimental curves should usually differ mainly in the existence of a relative flattening of the latter for higher intensities: thus equalities and inequalities, but not intensity ratios, should be correctly reproduced.

Intensities in $^1S\rightarrow{}^1S$ *transitions* ($\sigma'=\sigma''=0$). The applicability of Eqs. (1) and (2) to bands involving $^1S\rightarrow{}^1S$ transitions has been discussed in the first section. Certain minor points remain to be considered. Although in the case of the HCl bands at 3.46μ the work of Kemble and Bourgin confirms the predicted greater intensity of the R branch in absorption, due to the Boltzmann factor, there are other infra-red absorption bands, as pointed out by Fowler,[11] in which the P branch appears to be the stronger. Aside from the possibility of experimental error, this may be ascribed (as Oppenheimer has intimated[16]) to a variation of the a factor of Eqs. (1) and (2) due to molecular vibration (cf. above, p. 398), in such a way as to favor the P branch, even to the extent of making it stronger than the R branch by overcoming the contrary effect of the Boltzmann factor.

The excess intensity of the P over the R branch in the CuH bands is considerably greater[11] than that predicted by the theory because of the effect of the Boltzmann factor alone. On the latter basis, the strongest P line should be about 7.5% more intense than the strongest R line, while according to Frerich's data,[20] the excess is about 27%, 13%, or 11%, in three different bands. It seems possible that the discrepancy is due to the effect of molecular vibration. Such an effect is especially likely here on account of the high temperature (about 3400°C, assuming Eq. 1),[32] which causes the maximum intensity in each branch to lie at relatively high values of j.

Intensities in $^1P \rightarrow {}^1S$ *transitions* ($\sigma' = 1, \sigma'' = 0$) *in helium bands.* The class of bands under discussion is represented, according to recent conclusions of the writer,[7,33] by a large number of helium bands, the "series" bands of Fowler and Curtis and Long. Although only eye estimates of intensity are available, these exist for so many bands that a good comparison with theory is possible. Such a comparison is made in Fig. 1. Theoretical curves (the intensities are of course on an arbitrary scale) are given in Fig. 1 only for two extreme cases $3^1P \rightarrow 2^1S$ and $7^1P \rightarrow 2^1S$: these and other (intermediate) cases differ, —but only slightly,—in respect to the value of E_0 as a function of j, in the Boltz-

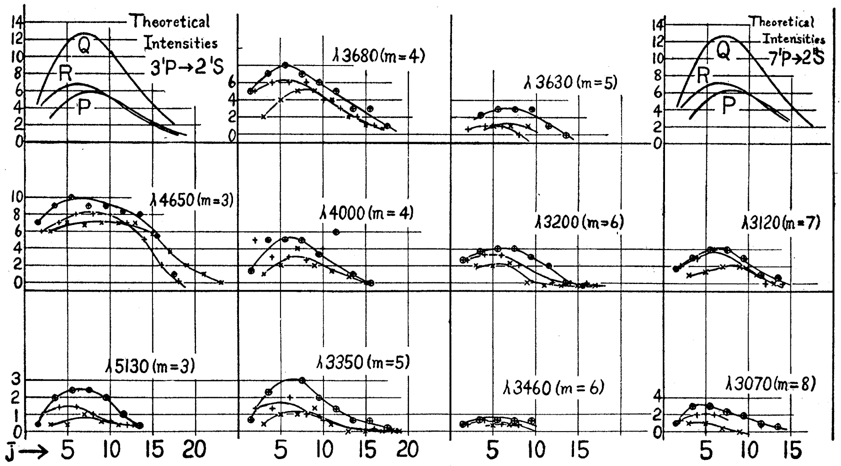

Fig. 1. Theoretical and observed intensities in $m\ {}^1P \rightarrow 2\ {}^1S$ helium bands of the "main" and "second" series. The theoretical intensities correspond to an assumed temperature of 700°C. The observed intensities for P, Q, and R branches, respectively, are denoted by $\times$, $\oplus$, and $+$.

---

[32] The distribution seems to be of the thermal equilibrium type. The assumption $T = 3640°K$ gives $j = 14+$ for the strongest P line and $j = 14-$ for the strongest R line, in agreement with observation.

[33] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 158 (1926).

mann factor. The temperature of 700°C assumed for all cases gives good agreement with the experimental intensity curves.[34]

The theoretical curves in Fig. 1 for the transition $3^1P \rightarrow 2^1S$ are based on the calculations given in Table I. Entirely analogous calculations apply for $7^1P \rightarrow 2^1S$ and other transitions. The theoretical intensities ($I_{\text{calc.}}$) are calculated by means of the equation $I = ie^{-E'/kT}$ (for emission bands E_0 of Eq. 1 is E'). The E' values (in wave-number units) are from Curtis and Long's analysis of the λ4650 ("main series") band.[35] The E' values are nearly the same for the "second series"

TABLE I

Calculation of theoretical intensities for helium band λ4650($3^1P \rightarrow 2^1S$ *transition*), *assuming* $t = 700°C$ ($kT = 679$). The *absolute* values of i and I are without significance here; the $I_{\text{obs.}}$ values, being eye estimates, are furthermore not directly proportional to true intensities. The values of E' and kT are in wave-number units.

P and R Branches

$j'-\frac{1}{2}$	E'	$e^{E'/kT}$	Designation*	i	$I_{\text{calc.}}$	$I_{\text{obs.}}$ λ4650	$I_{\text{obs.}}$ λ5130	Designation*	i	$I_{\text{calc.}}$	$I_{\text{obs.}}$ λ4650	$I_{\text{obs.}}$ λ5130
2	37	1.06	$R'(1)$	3	2.82	6	1	$P(2)$	2	1.90	6	0
4	136	1.22	2	5	4.08	7	1+	3	4	3.27	7	0
6	292	1.54	3	7	4.55	8	1+	4	6	3.90	7−	1
8	503	2.10	4	9	4.30	8	1	5	8	3.83	7	1−
10	770	3.11	5	11	3.54	8	1−	6	10	3.22	7	0
12	1090	5.00	6	13	2.60	7	0	7	12	2.40	7	0
14	1464	8.65	7	15	1.73	5	–	8	14	1.62	6−	–
16	1889	16.1	8	17	1.06	2	–	9	16	0.99	4−	–
18	2365	33	9	19	0.58	1−	–	10	18	0.55	2	–
20											1	
22											0	

* In the notation of Curtis and Long.

Q Branch

Designation	$j'-\frac{1}{2}$	E'	$e^{E'/kT}$	i	$I_{\text{calc.}}$	$I_{\text{obs.}}$ λ4650	$I_{\text{obs.}}$ λ5130
$Q(1)$	1	9	1.01	3	2.96	7	0
2	3	80	1.12	7	6.23	9	2
3	5	208	1.36	11	8.12	10	2+
4	7	391	1.78	15	8.43	9	2+
5	9	631	2.54	19	7.49	9	2
6	11	932	3.94	23	5.84	8+	1
7	13	1272	6.5	27	4.15	8	0
8	15	1677	11.8	31	2.60	6	–
9	17	2141	23.5	35	1.49	1	–

---

[34] The intensity estimates on the bands corresponding to the most excited electronic states were made on a different set of exposures than for the remaining bands and the ${}^1D \rightarrow {}^1P$ and ${}^1S \rightarrow {}^1P$ bands discussed below, so that a different value of T might have been anticipated; the change seems, however, to be within the errors of the data.

[35] The E' values are essentially those given in Table VII of Curtis and Long's paper (Proc. Roy. Soc. **108A**, 513, 1925), except for an additive constant $-B\sigma^2$ (since $\sigma = 1$, $-B\sigma^2 = -B = -7$), due to the assumption here of the form $B\ (j^2 - \sigma^2)$ in place of Bj^2 used by Curtis and Long.

bands as for the corresponding "main series", so that practically the same theoretical curves are applicable to both. The i values are as given by Eq. (5). The theoretical curves are obtained by plotting the calculated I values against j. Of course we are really dealing with a discontinuous function, so that the continuous curves are of significance only as an aid to the eye in appreciating the relation of the points through which they are drawn. Furthermore, in drawing the curves (both theoretical and experimental) the points corresponding to alternate j values (which strictly should be plotted with zero intensity) have been disregarded. This matter has been discussed in a previous section (p. 400).

A comparison of the theoretical and experimental curves on the above basis, bearing in mind the various possible causes of distortion and error in the experimental curves, indicates that the two are in essential agreement. Considering individual bands, the agreement is not always very good, but the deviations seem irregular, and most of them disappear if one replaces the individual curves in imagination by an average curve. Individual deviations may be only apparent and due to the crudeness of the method of recording intensities, or they may in some cases be due to perturbations (also, see below).

The agreement with theory may be described under the following headings:

(1) The Q branch is always the strongest, and, so far as can be seen from the data, may well actually be twice as strong as either of the other two branches, as predicted; the latter relation is indicated especially in the bands of low intensity, where the estimates of blackening are more nearly proportional to true intensity.

(2) The values of j for the *strongest line* in each branch are on the whole in the correct order $P>Q>R$, and differ by the correct amounts; these j_{max} values are moreover practically the same in all the bands, showing that the same effective temperature applies to all.

(3) The R branch is always markedly stronger than the P branch for small j values (the first R line is approximately twice as strong as the first P line, although j is only two thirds as great), while for large j values the two branches are asymptotically about equal in intensity. The first R line is about equal in intensity to the first Q line.

In spite of the crudity of the intensity data, the experimental curves are thus unmistakably of the predicted type for $\sigma'=1$, $\sigma''=0$, and equally unmistakably are different from the predicted types for any other pair of values of σ' and σ'', even for the same value of $\Delta\sigma$ (cf. curve for $\sigma'=2$, $\sigma''=1$, in Fig. 2). The agreement is all the more remarkable in view of the fact that alternate lines in each branch are missing, and in view of the existence of rotational doubling, since neither of these facts is anticipated by the theory. It is important to note that the agreement would not exist if the *j* values had not been assigned on the assumption of alternate missing lines.

Taken together with the evidence previously given,[7] the present results seem to constitute conclusive evidence in favor of the interpretation of the He_2 bands given in previous papers.[33,7]

The fact that the agreement with theory is not disturbed by the circumstance that the *Q* lines arise from *A* rotational sub-states and the *P* and *R* lines from *B* sub-states indicates (among other things) that the two sub-states have equal a priori probabilities (cf. discussion above, p. 399)

There seem nevertheless to be certain systematic minor deviations from the theoretical curves. For the bands involving highly excited initial electronic states, there is a tendency toward more rapid decrease of intensity for high *j* values than the theory calls for. For the most excited states, there even seems to be a shift, for the line of maximum intensity in each branch, toward a lower value of *j* than predicted. These effects can probably be attributed to a marked instability of molecules having high *j* values, especially for the higher electronic states (such instability is also indicated by the setting in of a rapid diminution in the rate of growth of the spacing of the rotational energy levels). Due to this instability, such molecules are presumably reduced in numbers below the proportions corresponding to statistical equilibrium. The question of instability has been discussed by Curtis.[36]

Other $^1P \rightarrow {}^1S$ *transitions: the* AlH *Bands.* Primarily on the basis of missing lines, the known AlH band system has been classified[7] as corresponding to a $^1P \rightarrow {}^1S$ electron transition. The bands should therefore show intensity relations similar to those in the He_2 bands just discussed, but without the complication of alternate missing lines. According to Eriksson and Hulthén,[37] the *Q* branch is approximately twice as strong as the *P* or *R* branch, as it should be for a $^1P \rightarrow {}^1S$ (or $^1S \rightarrow {}^1P$) transition. The intensities (eye estimates) given by Eriksson and Hulthén give indications of the expected superior intensity of the *R* as compared with the *P* branch for low *j* values; the same is true of the data of Mörikofer[38] on the same bands (for "Form *I*" of the discharge).

A more definite confirmation of the predicted intensity relations is obtained by a study of a photometer curve of the $\lambda 4354$ ($n' \rightarrow n'' = 1 \rightarrow 1$) band as given by Eriksson and Hulthén. So far as can be seen, the intensities are in agreement with prediction (for thermal equilibrium at a fairly high temperature), but it does not seem worth while to make a detailed comparison, since there is much superposition of lines

---

[36] W. E. Curtis, Proc. Roy. Soc. **103A**, 315 (1923).

[37] G. Eriksson and E. Hulthén, Zeits. f. Physik **34**, 775 (1925). In regard to the intensity of the *Q* branch, cf. footnote on p. 777.

[38] W. Mörikofer, Dissertation Basel, 1925.

from different branches. The peaks corresponding to the first line of the *R* branch ($\bar{j}=1$) and the second line of the *P* branch ($\bar{j}=3$) are, however, fairly free from neighboring peaks,[39] and their intensities are seen to be roughly equal, in agreement with the theoretical prediction that $i=2$ for both (cf. Eq. 5). This, in connection with the evident superiority of intensity of the *Q* branch, is good evidence that the intensity relations are of the predicted type. The observed relations may be contrasted with those predicted for the case $\sigma'=\sigma''=0$, where the intensities of the lines mentioned should be in the ratio 1 : 3, and with those for $\sigma'=0$, $\sigma''=-1$, where the *R* line in question should be *absent*, and the *P* line should have $i=4$.

Intensity relations in $^1D\rightarrow{}^1P$ *transitions* ($\sigma'=2$, $\sigma''=1$): *the helium band* λ 5733. In previous papers[7,33] it was concluded that He_2 λ5733 is the (only known) representative of a $^1D\rightarrow{}^1P$ transition, with $\sigma'=2$, $\sigma''=1$. The intensity data in Table II below are eye estimates by Curtis.[40] The corresponding theoretical intensities are obtained in much the same way as for the $^1P\rightarrow{}^1S$ transitions in He_2, using the relation $I=ie^{-E'/kT}$, calculating the i values from Eq. (5), and assuming the same effective temperature (700°C) as in the previous case, since the photographs were made under the same conditions. In one respect the procedure is different, due to the fact that the λ5733 band has six branches (two of each type), as compared with three for the bands previously discussed; this is due to the occurrence of rotational doubling for both ^1D and ^1P states.[7] As in the $^1P\rightarrow{}^1S$ bands, each branch has alternate lines completely missing. This, however, occurs in such a way that one *P*, one *Q* and one *R* line is present for each value of j' or j'' (above $j'_{\text{min.}}$ or $j''_{\text{min.}}$), and in Fig. 2 all these lines have been plotted in a continuous series for the experimental as well as for the theoretical curves. The theoretical intensities of course lie (nearly) on a continuous curve, since the theory makes no provision for rotational doubling, except in so far as this affects the value of $E'(j)$[41]. The fact that the observed intensities also lie on smooth curves in spite of the fact that the intensities for alternate values of j correspond to different rotational sub-states, indicates that (as in the "series" bands) the two substates (*A* and *B*) are alike in respect to their a priori probabilities, etc. If the present discussion does not make these points clear, a study of Fig. 2 and Table II, in connection with the discussion of He_2 λ5733 in ref. 7, should do so.

From Fig. 2 and Table II it is evident that the substitution of $\sigma'=2$ for $\sigma'=1$, without any change in $\Delta\sigma$, is enough to produce a very great

---

[39] In the notation of Eriksson and Hulthén, these lines are *R*(1) and *P*(4).

[40] W. E. Curtis, Proc. Roy. Soc. **101A,** 38 (1922).

[41] As a matter of fact, the values of E' (j) fall into two sets which are sufficiently different so that the theoretical curve should not be quite smooth (cf. Table II); for convenience, however, a smooth curve has been drawn in Fig. 2.

TABLE II

Calculation of theoretical intensities for helium band λ5733 ($3^1D\rightarrow 2^1P$ *transition*) *assuming* $t=700°\text{C}$

See note at top of Table I. The "Designations" are those given by Curtis,[40] and also used by Kratzer. For the experimental I data, see Fig. 2 or ref. 40. The E' values for $j'=2\frac{1}{2}$, $4\frac{1}{2}$, $6\frac{1}{2}$, $\cdots$ are $F'_A(j)$ values. These values were obtained as follows: (*a*) $E'(2\frac{1}{2})$ and $E'(3\frac{1}{2})$ were first calculated from $E\backsim B(j^2-\sigma^2)=B(j^2-4)$, using $B_A=B_B=7.56$, $\sigma=2$, as given in ref. 7; (*b*) then making use of the Δ_2F' values given by Kratzer (Zeits. f. Physik **16**, 353, 1923), the remaining E' values were obtained by suitable summation (by definition,—see ref. 6, Eqs. 10,—$\Delta_2F(j)=F(j+1)-F(j-1)$). E. g., $E'_A(4\frac{1}{2})=E'_A(2\frac{1}{2})+\Delta_2F'_A(3\frac{1}{2})$; $E'_A(6\frac{1}{2})=E'_A(4\frac{1}{2})+\Delta_2F'_A(5\frac{1}{2})$, etc., while $E'_B(5\frac{1}{2})=E'_B(3\frac{1}{2})+\Delta_2F'_B(4\frac{1}{2})$, etc. The quantities here designated $\Delta_2F'_A(3\frac{1}{2})$, $\Delta_2F'_A(5\frac{1}{2})$, $\cdots$, and $\Delta_2F'_B(4\frac{1}{2})$, $\Delta_2F'_B(6\frac{1}{2})$, $\cdots$, are respectively identical with Kratzer's $\Delta F_2(1)$, $\Delta F_2(2)$, $\cdots$, and $\Delta F_1(2)$, $\Delta F_1(3)$, $\cdots$ (cf. Kratzer's Table 6, p. 359). The E' values for $j'=17\frac{1}{2}$ to $20\frac{1}{2}$ were estimated approximately by extrapolation.

$j'-\frac{1}{2}$	E'	$e^{-E'/kT}$	Designation	i	I
2	17	1.03	$R'(1)$	6	5.85
3	62	1.10	$R\ (2)$	6 2/3	6.09
4	122	1.19	$R'(2)$	7 1/2	6.30
5	199	1.34	$R\ (3)$	8 2/5	6.27
6	287	1.53	$R'(3)$	9 1/3	6.10
7	395	1.79	$R\ (4)$	10 2/7	5.75
8	510	2.12	$R'(4)$	11 1/4	5.31
9	650	2.60	$R\ (5)$	12 2/9	4.70
10	790	3.20	$R'(5)$	13 1/5	4.13
11	963	4.14	$R\ (6)$	14 2/11	3.43
12	1126	5.26	$R'(6)$	15 1/6	2.88
13	1332	7.10	$R\ (7)$	16 2/13	2.28
14	1516	9.3	$R'(7)$	17 1/7	1.84
15	1756	13.2	$R\ (8)$	18 2/15	1.37
16	1958	17.8	$R'(8)$	19 1/8	1.07
17	(2232)	27.1			
18	(2449)	37			
19	(2755)	60			
20	(2987)	82			

$j'-\frac{1}{2}$	Designation	i	I	Designation	i	I
2	$Q_2(1)$	3 1/3	3.25	$P\ (2)$	2/3	0.65
3	$Q_1(1)$	5 5/6	5.33	$P'(2)$	1 1/2	1.37
4	$Q_2(2)$	8 1/10	6.81	$P\ (3)$	2 2/5	2.02
5	$Q_1(2)$	10 4/15	7.66	$P'(3)$	3 1/3	2.48
6	$Q_2(3)$	12 8/21	8.09	$P\ (4)$	4 2/7	2.80
7	$Q_1(3)$	14 13/28	8.08	$P'(4)$	5 1/4	2.94
8	$Q_2(4)$	16 19/36	7.80	$P\ (5)$	6 2/9	2.94
9	$Q_1(4)$	18 26/45	7.15	$P'(5)$	7 1/5	2.77
10	$Q_2(5)$	20 34/55	6.44	$P\ (6)$	8 2/11	2.56
11	$Q_1(5)$	22 43/66	5.48	$P'(6)$	9 1/6	2.22
12	$Q_2(6)$	24 53/78	4.69	$P\ (7)$	10 2/13	1.93
13	$Q_1(6)$	26 64/91	3.76	$P'(7)$	11 1/7	1.57
14	$Q_2(7)$	28 76/105	3.09	$P\ (8)$	12 2/15	1.31
15	$Q_1(7)$	30 89/120	2.33	$P'(8)$	13 1/8	0.99
16	$Q_2(8)$	32 103/136	1.84	$P\ (9)$	14 2/17	0.79
17	$Q_1(8)$	34 118/153	1.28	$P'(9)$	15 1/9	0.56
18				$P\ (10)$	16 2/19	0.45
19				$P'(10)$	17 1/10	0.29
20				$P\ (11)$	18 2/21	0.22
				$P'(11)$		

change in the quantitative theor[illegible]al intensity relations. The *observed* intensities lie on curves which a[illegible] very closely in form (including the position of the line of maximum [illegible]nsity) with the theoretical curves. The predicted very high intens[illegible] of the first few R lines and the corresponding very low intensity [illegible]he first P lines are verified. These agreements give powerful support to the interpretation of the band as having $\sigma'=2$, $\sigma''=1$.

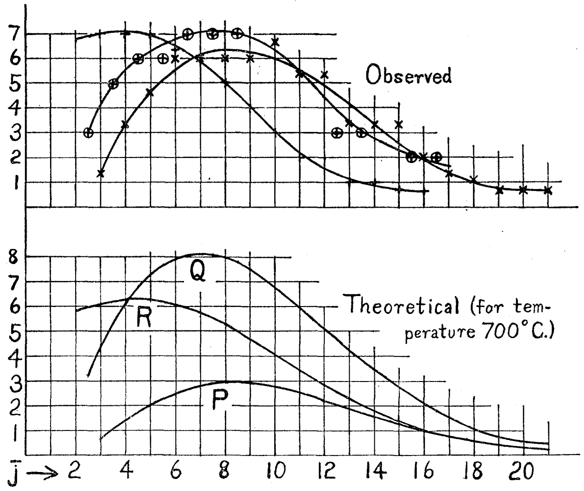

Fig. 2. Intensity relations in λ5733 helium band ($3\ ^1D \rightarrow 2\ ^1P$). The "observed" points are Curtis's estimates,[40] except that for the P lines Curtis's estimates have been multiplied by 2/3 (cf. text). Points where two or more lines are superposed have been omitted. Thus Q_1 (5), Q_2 (7), and R' (1) are all superposed (the calculated position of Q_2 (7) is 17467.85, in sufficiently good agreement with that of an observed line for which $\nu=17467.30$). The previously unassigned line $\nu=17471.64$ (int. 2) is evidently Q_2 (8). It is possible that Q_1 (8) is present and superposed on R' (2). It seems probable that the apparent abnormally high intensity of P' (5) is due to the superposition of a line not belonging to the band.

In certain respects the observed intensities of Fig. 2 and Table II seem to disagree with the theory: the Q branch as a whole is relatively too weak and the P branch is much too strong, in spite of the fact that in Fig. 2 Curtis's intensity estimates[38] for the P branch have been multiplied by a factor 2/3 before plotting (partial justification for this procedure is obtained by an examination of the reproduction given by Curtis, in which the P branch appears relatively considerably weaker than Curtis's data indicate). It seems possible that the apparent high intensity of the P branch may be largely due to change of plate sensitivity with wave-length (the P branch extends from λ5821 to λ5748, the Q branch from λ5733 to λ5716, the R branch from λ5724 to λ5646, and in this part of the spectrum, rapid changes of plate sensitivity occur for some types of plates; Curtis does not state what type of plate he used). It also seems possible that a different intensity scale may have been (more or less unconsciously) used for the eye estimates in the different branches. The high intensity of the P branch might also be due partly to variability in the a factor of Eq. (5). Further experimental work is needed.

Intensity relations in $^1S\rightarrow{}^1P$ *transitions* ($\sigma'=0$, $\sigma''=1$)*: helium bands* λ4546 *and* λ6400. The helium bands λ4546 and λ6400 correspond to transitions $4^1S\rightarrow 2^1P$ and $3^1S\rightarrow 2^1P(\sigma'=0,\ \sigma''=1$ in both cases), according to the conclusions of previous papers.[7,33] Eye estimates of intensity[40] are available. In Table III these are compared with the theoretical intensities, assuming $t=700°\text{C}$ as for the other helium bands, but using Eq. (6) in calculating the i values. The predicted intensities are similar to those for $^1P\rightarrow{}^1S$ transitions except that here the P branch should be stronger than the R branch throughout its course, but especially at the beginning.

TABLE III

Intensities in helium bands λ4546 *and* λ6400 ($4^1S\rightarrow 2^1P$ *and* $3^1S\rightarrow 2^1P$ *transitions*), *assuming* $t=700°C$.

See note at head of Table I. The numbers under the headings R, Q, and P, are Curtis's designations[40] for the lines of the three branches.

$j'-\frac{1}{2}$	E'	$e^{E'/kT}$	R	i	$I_{\text{calc.}}$	$I_{\text{bos.}}$ λ4546	λ6400
1	16	1.02					
3	88	1.14	1	2	1.76	3	(8)
5	218	1.38	2	4	2.90	3	8
7	405	1.82	3	6	3.30	3	9
9	648	2.60	4	8	3.08	3	10
11	947	4.03	5	10	2.48	3	6
13	1300	6.78	6	12	1.77	1	3
15	(1707)	12.3					

$j-\frac{1}{2}$	Q	i	$I_{\text{calc.}}$	$I_{\text{obs.}}$ λ4546	λ6400	P'	i	$I_{\text{calc.}}$	$I_{\text{obs.}}$ λ4546	λ6400
1	1	3	2.93	3	10	1	3	2.93	4	10
3	2	7	6.16	4	10	2	5	4.40	6	10
5	3	11	7.99	6	10	3	7	5.08	6	10
7	4	15	8.26	6	10	4	9	4.96	6	10
9	5	19	7.30	6	10	5	11	4.23	6	10
11	6	23	5.70	5	10	6	13	3.22	6	10
13	7	27	3.98	4	8	7	15	2.21	3	—
15	8	31	2.51	3	3	8	17	1.38	1	

The observational data are not very satisfactory. For λ6400 the recorded intensities indicate that the plate was overexposed, no distinction being made between lines exceeding a certain intensity. However, in both λ6400 and λ4546 the predicted relatively low intensity of the

R branch is verified, and for λ4546 the data on the Q branch indicate agreement with the theory.

In both bands, as in He_2 λ5733, the recorded intensities of the P branch lines are greater, relatively to those of the Q branch, than one would expect from the theory. If these deviations are real, they might perhaps be ascribed to the effect of nuclear vibration (but $n'=n''=$ only $\frac{1}{2}$, probably), or to a lack of rigid binding of σ(cf. above, p. 398). Further more careful intensity measurements will be needed before definite conclusions can be reached.

Even with the present data there can, however, be no doubt that the bands have an intensity distribution entirely different from those in $^1P\rightarrow{}^1S$ and $^1D\rightarrow{}^1P$ bands, and differing from these in at least qualitatively the correct way.

New data on helium bands: note added in proof. McLennan, Smith, and Lea have recently published intensity data on a number of helium bands at low temperatures (walls of discharge tube at 21°K., 85°K., and 300°K. in various runs).[42] The data on the relative intensities of the P and R branches are in excellent agreement with the theory for the ($^1P\rightarrow{}^1S$) bands λλ4650, 5130, 3680, 4000, 3630, and for the ($^1S\rightarrow{}^1P$) bands λλ4546 and 6400. In the latter case, the new data furnish a welcome supplement to those of Table III, although the absence of data on the Q branches is unfortunate. In the former case, the Q branches are more intense than the P and R branches, as expected, although apparently not twice as intense; however, it is not clear whether the data are supposed to be quantitative. The data for λ5733 ($^1D\rightarrow{}^1P$), on the P and R branches only, are in poorer agreement with the theory than are those of Curtis.—In respect to the values of j for the strongest line of each branch, a sample calculation indicates that the observed distributions correspond to the low temperatures used. But the branches fade out much too slowly with increasing j; this probably means that a considerable fraction of the molecules were in a region of relatively high effective temperature.

Intensity relations in $^1S\rightarrow{}^1P$ transitions: CO *Angstrom bands.* In a previous paper,[6] the CO band system of Ångström and Thalen has been interpreted as due to an electron transition for which $\sigma'=0$, $\sigma''=1$. Photographs of these bands were recently taken by the writer in the second order of the 21 foot concave grating at Harvard University. The bands were excited by a transformer discharge in CO_2 at low pressure. The photographs were taken in connection with a study of the Zeeman effect and were not intended for photometric work; it was found later that the exposures without field offered valuable material for the present work.

---

[42] J. C. McLennan, H. G. Smith, and C. A. Lea, Proc. Roy. Soc. **113A**, 183 (1926).

In order to obtain more accurate data than would be secured by eye comparisons, a photometer curve was run on the $\lambda 4835$ band ($n'=0$, $n''=1$), with the kind assistance of Dr. H. A. Barton, using the microphotometer at Princeton University. The galvanometer readings (proportional to intensity of light transmitted through the plate) for the center of each band line were then taken from the curve. Each such reading was then subtracted from the "fog" reading for a neighboring region between band lines. The results were plotted against j in Fig. 3,

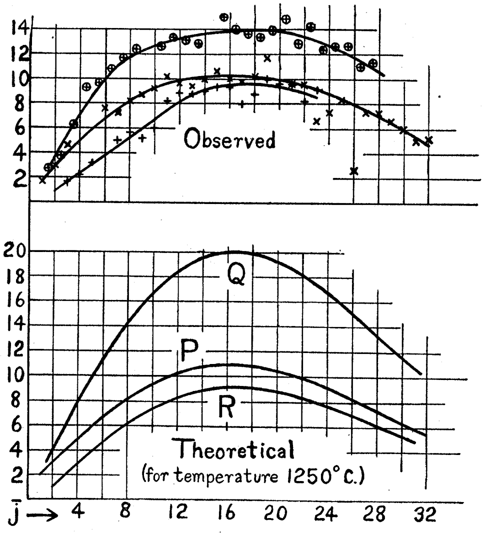

Fig. 3. Intensity relations in CO Angstrom and Thalen band ($^1S\rightarrow{}^1P$) at $\lambda 4835$.

omitting, however, data on lines which were imperfectly resolved by the photometer. Results obtained in the above manner are similar in meaning to eye estimates, but more reliable.[43]

Bearing in mind the nature of the data, the agreement between the theoretical and experimental curves as shown in Fig. 3 (assuming an effective temperature of 1250°C) is very satisfactory throughout the range of j values for which data were obtained. As predicted, the P branch is stronger than the R branch throughout its course, and much stronger at the beginning, while the Q branch is stronger than either the P or the R branch. As in other cases, however, the P branch seems to be slightly stronger than is predicted with the assumption that a in Eq. (6) is constant; as already discussed on p. 398, this effect may

---

[43] By making assumptions as to the characteristics of the plate, semi-quantitative intensity data might have been obtained, but this did not seem worth while at the time on account of the doubtfulness of the necessary assumptions.

perhaps be attributed to vibration of the molecule.[44] The extent of the agreement between theory and experiment can best be verified from the theoretical curves by picking out various pairs or sets of lines whose intensities should be equal, and comparing with the experimental curves. Examination of other CO bands of the same system disclosed similar intensity relations, but no detailed measurements were made.

INTENSITY RELATIONS IN BANDS INVOLVING DOUBLET AND HIGHER ELECTRONIC STATES

Eqs. (4)–(6) may be expected to hold in general for odd as well as for even molecules, for bands involving, in both the initial and final states, rotational terms of the form $B(j^2-\sigma^2)+\cdots$. Thus Eq. (4) should apply to ${}^2P_1\rightarrow{}^2P_1$ and ${}^2P_2\rightarrow{}^2P_2$ transitions; this is confirmed by experiment, as will be shown by Barton, Jenkins, and the writer in a later paper. Similarly in ${}^2D\rightarrow{}^2D$, ${}^3P\rightarrow{}^3P$ and other combinations, Eqs. (4)–(6) should hold.

When rotational terms of the form $B(j-\rho)^2+\cdots$ are involved in one or both electronic states, Eqs. (4)–(6) are inapplicable and it is not obvious what relations should take their place. Nevertheless, the observed intensity relations seem to be at least qualitatively in agreement with these equations. Thus for ${}^2S\rightarrow{}^2S$ transitions (violet CN band type, type (*c*) of the first section of this paper) the obvious structure and intensity relations are the same as for ${}^1S\rightarrow{}^1S$ (type *b*) transitions, except that each line is a doublet, due to the presence of a ρ with approximately the values $\pm\frac{1}{2}$. In ${}^2P_1\rightarrow{}^2S$ and ${}^2P_2\rightarrow{}^2S$ transitions ($j_e'=\sigma=\frac{1}{2}$ or $\frac{3}{2}$, $j_e''=\rho=\pm\frac{1}{2}$), the intensity distributions in the various branches in known cases (ZnH, CdH, and HgH bands) shows a resemblance to those for other transitions such as ${}^1P\rightarrow{}^1S$ where σ decreases during emission.

The writer wishes to express his appreciation of the stimulating discussion and valuable criticism of Professor E. C. Kemble.

WASHINGTON SQUARE COLLEGE,
NEW YORK UNIVERSITY,
November 13, 1926.

---

[44] The anomalous intensity of the P line $j=26$ (perhaps also of other lines) is due to a perturbation; this line is also shifted a considerable distance from its expected position.