DECEMBER, 1926 PHYSICAL REVIEW VOLUME 28

# ELECTRONIC STATES AND BAND-SPECTRUM STRUCTURE IN DIATOMIC MOLECULES
## II. SPECTRA INVOLVING TERMS ESSENTIALLY OF THE FORM $B(j^2-\sigma^2)$

By Robert S. Mulliken

### Abstract

**Properties of rotational terms of the form** $B(j^2-\sigma^2)$.—Evidence is presented to show that the AlH, $He_2$, and certain other bands involve rotational terms essentially of the form $B(j^2-\sigma^2)$, and are in agreement with the postulates of a previous paper.[1] Since terms of this form have not hitherto been recognized *in practice*, their chief empirical properties, as shown by the bands discussed below, are now summarized. (1) There are in general two values of the rotational energy term $F(j)$ for each $j$ value. This type of rotational doubling has previously been confused with that which occurs, due to $\pm\epsilon$ (where $\epsilon=|\rho|$), when $F(j)$ is essentially of the form $B(j-\rho)^2$. In the special case where $\rho$ and $\sigma$ are both zero ($^1S$ states), all rotational doubling is absent. (2) The two sets of $F(j)$ values, in doubling of the $\sigma$ type, in general differ in respect to the values of $B$ and of a small "secondary" $\rho$ whose presence must, at least formally, be admitted; thus $F_i(j)=B_i[(j-\rho_i)^2-\sigma^2]+\cdots$ ($i=A$ or $B$), with $\epsilon<\frac{1}{2}$, or usually $\ll\frac{1}{2}$, in practice; a slight difference in the electronic term values may also occur (as e.g., in the $He_2$ bands). (3) In general, there are six branches in combinations of two $\sigma$-type terms (cf. Eqs. (2) of text); in the $P$ and $R$ branches, combinations occur only between like rotational terms ($F'_A\rightarrow F''_A$, and $F'_B\rightarrow F''_B$), while in the $Q$ branches, "crossing over" always occurs ($F'_A\rightarrow F''_B$ or $F'_B\rightarrow F''_A$). (4) In the special case of $^1P-{}^1S$ and $^1S-{}^1P$ combinations (cf. Eqs. (1) and Fig. 1 of text), there are only three branches, due to the existence for the $^1S$ electronic state of only one rotational state for each value of $j$ (these states have the properties of $F_B$ states); apparent "combination defects" in $P$-$Q$-$R$ combinations result here from the $Q$ crossing over phenomenon. (5) In $^2S-{}^2P$ and $^2P-{}^2S$ transitions, the intercombination of the $\rho$-type $^2S$ term with the $\sigma$-type $^2P_1$ or $^2P_2$ term gives rise to a special band structure (with six branches) in which for a frequent limiting case there is a practically complete coalescence of one of the $P$ with one of the $Q$ branches, and of one of the $R$ branches with the other $Q$ branch (cf. Eqs. (8), (8A), and (8B) of text). The existence of these band-types is strong evidence for the reality of the $\rho$ values $+\frac{1}{2}$ and $-\frac{1}{2}$ for $^2S$ states, and so affords additional confirmation of Kratzer's interpretation of the violet CN bands ($^2S-{}^2S$ transition) as adopted in ref. 1.

**The CO, AlH, and $He_2$ bands.**—Assuming $\rho=0$, $\sigma=1$ for $^1P$ states, it was shown in ref. 1 that the structure and missing lines of the CO Ångstrom bands are in agreement with the classification $^1P-{}^1S$ given by Birge. The AlH bands are now shown to fall under the classification $^1S-{}^1P$, and it is predicted that the fourth positive CO bands, designated as $^1S-{}^1P$ by Birge, will have the corresponding structure and missing lines.—By adopting the assumption (due to Mecke) that alternate lines are missing in each branch, it is shown

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

that the three-branch "series" bands of helium are of the $^1S-{}^1P$ type and the three-branch bands λ6400 and 4546 of the $^1P-{}^1S$ type, while the six-branch band λ5733 appears as the (only known) representative of the $^1P-{}^1D$ type. Revised values of various constants of the $He_2$ molecule in its different electronic states are given in Table I. To account for the alternate missing lines, a system of alternate suppressed rotational levels (cf. Fig. 2) is assumed. The correctness of this system is supported by several lines of evidence in addition to the satisfactory interpretation of the band structures; e.g., it correctly predicts the absence of $^1S-{}^1S$ and $^1P-{}^1P$ transitions in $He_2$. The relation of the excited states of $He_2$ to those of He is discussed briefly.

**Resonance series and the band spectra of the alkalies and the halogens.** The fluorescent radiation emitted by a molecule after excitation by absorption of monochromatic light consists under suitable conditions of a series ("resonance series" of Wood) of roughly equidistant groups of band lines, corresponding to a series of final vibrational states. According to the present analysis, various transitions in even molecules should yield resonance series of the following types: $^1S-{}^1S$, *P-R* doublets; $^1P-{}^1P$ (or $^1D-{}^1D$, etc.), *P-Q-R* triplets but with the *Q* member usually too weak to be noticed; $^1P-{}^1D$, $^1D-{}^1P$, $^1P-{}^1S$, etc., *P-Q-R* triplets; $^1S-{}^1P$, doublet series (*P*,*R*) for some exciting wave-lengths and singlet series (*Q* only) for others. The visible $I_2$ absorption bands give rise to *P-R* doublets (interpreted as such by Lenz), so that they (and by analogy the corresponding $Br_2$ and $Cl_2$ bands) are probably $^1S-{}^1S$ (or perhaps $^1P-{}^1P$ or $^1D-{}^1D$). The $Na_2$ absorption bands in the green, giving both singlet and doublet resonance series, are probably $^1S-{}^1P$, and the same is probably true by analogy of most of the familiar alkali metal bands. In further support of this, there is no evidence, in the band structure, of electronic doublets such as appear in the atomic transitions $^2S-{}^2P_{1,2}$. The relation of the electronic states of $Na_2$ to those of Na is briefly discussed.

**Other band spectra.**—Although no detailed analyses are available, the evidence indicates that the red CN, BOα, and $CO^+$ comet tail bands (also the doublet alkaline earth halide bands?) have a structure (cf.(5) under "Properties . . . . ," above) essentially the same as that of the ZnH, CdH, and HgH bands, and characteristic of the transition $^2S-{}^2P_{1,2}$. The "combination" bands of BO and $CO^+$ and the NO third positive bands (presumably also Jevons' SnCl bands) probably have a similar structure characteristic of $^2P_{1,2}-{}^2S$ transitions. Predictions are given for the structure of $^2P-{}^2D$ bands; these should differ from all bands now on record in having $T'$ and $T''$ both integral.—The OH, CH and MgH bands are briefly discussed following Table II, which gives a condensed summary of $T$, $\rho$ and $\sigma$ values, and electronic transitions, for the band types discussed here and in ref. 1. Table II shows that *in all known cases, $j_e$ appears essentially as $\sigma$ in P and D states, but as $\pm\epsilon$ in S states* (for $^1S$ states $j_e=0$). A corollary is that $m$ is half-integral in known $S$ states, but not in $P$ or $D$ states.

## INTRODUCTION

In previous papers certain examples of band spectra involving rotational energy terms essentially of the form $B(j^2-\sigma^2)$ have been discussed (CO Ångström bands,[1] ZnH, CdH, and HgH bands)[2]. In section *A* of the present paper, the structures of a number of further

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

examples, involving singlet electronic states and due to even molecules, are interpreted; while in section $B$ additional examples due to odd molecules and involving doublet electronic states are treated; in section $C$ the interpretations of this and preceding papers are summarized.

Frequent reference will be made below to the first paper of this series[1] for notation, definitions, etc.; this paper will always be referred to as I. The system of $j$ values used in the present paper is that adopted in I (cf. postulate *III*). As remarked in the "note added in proof" at the end of I, it is however likely that the true $j$ values are all $\frac{1}{2}$ unit lower than those here used.

## A. SPECTRA OF MOLECULES WITH AN EVEN NUMBER OF ELECTRONS

*General Relations.* From I, the following relations are always to be expected for combinations of terms of the form $B(j^2-\sigma^2)$, in even molecules: (*1*) $j_e=\sigma=0$ for $^1S$ states, 1 for $^1P$ states, 2 for $^1D$ states, etc. (cf. postulate *I* of I); (*2*) $j$=half-integral (cf. postulate *III* of I); (*3*) $j\sim T$, since $T=j-\rho$ by definition (cf. I, p. 491) and since we are assuming $\rho\sim 0$; (*4*) hence $j\sim T\sim\sigma+\frac{1}{2}$, $\sigma+1\frac{1}{2}$, $\sigma+2\frac{1}{2}$, $\cdot\cdot\cdot$, (cf. I, p. 488, section on missing lines); (*5*) $P$, $Q$, and $R$ branches are respectively $P$-, $Q$-, and $R$-form, since $\Delta T\sim\Delta j$ (cf. I, Eq. 5 and p. 492); (*6*) as a result of the presence of a $\sigma$ (either $\sigma'$ or $\sigma''$ or both,—cf. I, p. 488), $Q$ branches should always be present (in addition to $P$ and $R$ branches) except for the special case of $^1S-{}^1S$ transitions ($\sigma'=\sigma''=0$). To avoid possible misunderstanding, it should be remarked that the exact values of $\sigma'$ and $\sigma''$ have not been obtained from direct experimental evidence, but have been deduced from the missing lines, in connection with the postulates of I, as explained in I (cf. pp. 493-4).

In addition to these outstanding relations, there are a number of secondary but nevertheless important features which will now be stated in the form of probable empirical generalizations[3] in order to facilitate the discussion of individual spectra. The truth of these generalizations will at first be assumed, but will become increasingly evident as successive examples are considered.

Empirically, there are two rotational states for each value of $j$ when $\sigma>0$ ($^1P$, $^1D$, $\cdot\cdot\cdot$ states), but only one when $\sigma=0$. This rotational doubling superficially resembles that for terms of the type $B(j-\rho)^2$, where, however, the doubling is probably due (cf. I, discussion of violet CN bands, pp. 485-6) to a double sign of $\rho$ ($F_1$ and $F_2$ states). In the case of $\sigma$-type doubling, the two rotational states will now be designated $F_A$ and $F_B$.

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[3] The significance of these will be discussed in a subsequent paper.

As discussed in connection with CuH in I (pp. 498-9), $^1S$ states, where $\sigma = 0$, show no rotational doubling. One might then expect $^1S$ rotational states to act, in their combinatory properties with $^1P$ states, like a coalescence of $F_A$ and $F_B$ states. Actually, however, they are *unsymmetrically* single in that they give $Q$ combinations only with $F_A$ states and $P$ or $R$ combinations only with $F_B$ states, as expressed in Eqs. (1) and Fig. 1. These rules of combination are in fact here used as the basis for the *definition* of $F_A$ and $F_B$ states. This definition is intended to be so chosen that usually in practice $F_A(j) > F_B(j)$, to a certain extent paralleling the empirical relation $F_1(j+1) > F_2(j)$ which normally holds (cf. I, p. 486) for $\rho$-type terms when $\epsilon = \frac{1}{2}$; the relation $F_A(j) > F_B(j)$ is illustrated by the He$_2$ bands (cf. Eqs. 1 and 2 and $\rho$ and $B$ values of Table I), but for the AlH bands (cf. Eq. 4) $F_B(j) > F_A(j)$. In view of their combinatory properties, $^1S$ states are classified as $F_B$ states.[4] $^1S-{}^1S$ transitions, which might legitimately be included as special cases under the present discussion, have already been sufficiently treated in I (cf. pp. 498-500 and Eqs. 17).

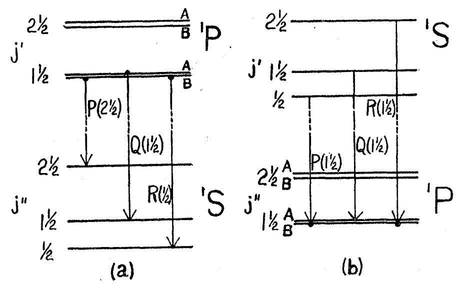

Fig. 1. Rotational energy levels and transitions for $^1S-{}^1P$ and $^1P-{}^1S$ electronic transitions. Only the lowest two or three levels are shown for each state. The only rotational transitions shown are those corresponding to the *first* possible line of each branch; additional band-lines are determined by analogous transitions between higher rotational levels.

$$^1S-{}^1P:\ R(j)=F_B'(j+1)-F_B''(j)\,;\ Q(j)=F_A'(j)-F_B''(j)\,; \qquad (1a)$$
$$P(j)=F_B'(j-1)-F_B''(j)$$

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[4] In $^1S-{}^1S$ transitions it is practically certain that "crossing over" does not occur for the $P$ and $R$ branches, since the terms are single and presumably of the same rotational type for all $^1S$ states. But in other transitions there is no *direct* evidence at present against the possibility that it is really the $P$ and $R$ branches, instead of the $Q$ branches for which crossing-over should be indicated in Eqs. (1) and (2); definite evidence could perhaps be obtained by a careful study of He$_2\lambda$5733. However, the analogy of the $^1S-{}^1S$ (and $^2S-{}^2S$, cf. I, p. 487) cases makes this very improbable, and it will therefore be assumed that crossing over occurs only in Q branches. A consequence of this assumption is the definite classification of $^1S$ states as $F_B$ states.

$$^1P-{}^1S:\ R(j)=F_B'(j+1)-F_B''(j)\,;\ \ Q(j)=F_B'(j)-F_A''(j)\,; \tag{1b}$$
$$P(j)=F_B'(j-1)-F_B''(j)$$

For the general case of combinations between two $\sigma$-type terms, Eqs. (2) are applicable (these equations also serve to *define* $Q_{AB}$ and $Q_{BA}$ branches):[5]

$$\begin{aligned} R_A(j)&=F_A'(j+1)-F_A''(j) &&;\quad R_B(j)=F_B'(j+1)-F_B''(j)\\ Q_{BA}(j)&=F_B'(j)-F_A''(j) &&;\quad Q_{AB}(j)=F_A'(j)-F_B''(j)\\ P_A(j)&=F_A'(j-1)-F_A''(j) &&;\quad P_B(j)=F_B'(j-1)-F_B''(j) \end{aligned} \tag{2}$$

Eqs. (1) and (2) illustrate a characteristic peculiarity of $Q$ branches,—a "crossing over" (adopting an expression due to Prof. R. T. Birge) from an $F_A$ to an $F_B$ term or vice versa.[4] A result of this is the occurrence of apparent "combination defects" when one attempts to obtain $\Delta_1F$ values by making use of $P$, $Q$, $R$ combinations (as in Eq. (20) of I); only $\Delta_2F$ combinations (cf. Eq. (18) of I) can be directly obtained.—Similar crossing over in $Q$ branches also occurs in other than pure $\sigma$-type bands (e.g. in the HgH type and probably[21] in the CH type bands).

The most usual difference between $F_A$ and $F_B$ terms is the occurrence of an apparent small "secondary" $\rho$ which differs in numerical value (sometimes also in sign) for $F_A$ and $F_B$.[6] In such cases the rotational term is therefore, strictly speaking, apparently of the *general* form of Eq. (8) of I, but the $\rho\sigma^2$ term (cf. Eq. (8*A*) of I) would usually be so small that it can be neglected. In addition to the occurrence of a small $\rho$, there is often an apparent slight difference in the $B$ values for $F_A$ and $F_B$ terms; and sometimes there is even a slight difference in the electronic term values ($F(e)$ of Eq. 3 of I), as is shown by the work of Curtis

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[5] What is essentially the term-scheme of Eq. (2) was first suggested by Mecke (Phys. Zeits. **26**, 219 (1925)) for $He_2\lambda5733$, except that Mecke implicitly assumed the terms to be of the $\rho$ type.

[6] The small secondary $\rho$'s which occur in $\sigma$-type terms are paralleled in the case of doubling of the true $\rho$ type by small *deviations* of $\epsilon$ from exact half-integers or integers as shown especially by Birge (cf. National Research Council Report on molecular spectra); without such small deviations there would be in fact no obvious doubling (cf. I, p. 486, violet CN bands). Also for $^1S$ states, where approximately $\rho=\sigma=0$, a small $\rho$ can occur (cf. I, ref. 52, CuH bands). It also seems possible (although not obviously open to experimental verification) that small secondary $\sigma$'s sometimes exist in the case of $\rho$-type states, and that there may be small deviations of $\sigma$ from exact integers or half-integers in $\sigma$-type states; these questions have been discussed to some extent previously in connection with the HgH type bands.[2]

It may be, however, that the use of a linear term in $j$, as introduced by Kratzer (cf. I, pp. 485–6), will prove to be more correct physically than the use of a "secondary $\rho$"; formally, the two are practically equivalent.

and Long on the $He_2$ bands (see below). $F(j)$ can then, formally at least, be represented by:

$$F_A(j)=B_A\left[(j-\rho_A)^2-\sigma^2\right]$$
$$F_B(j)=B_B\left[(j-\rho_B)^2-\sigma^2\right] \qquad (3)$$

CO *Bands.*[7] The Ångstrom CO bands have been discussed in I (pp. 501-2) and shown to fulfill all the requirements for a ${}^1P-{}^1S$ transition, except that Eqs. (1*b*) are replaced by simpler equations (Eqs. 19 of I) in which there is no separation of $F''$ into $F_A''$ and $F_B''$. We are free, however, to suppose that a very small separation is actually present, so that these bands need not be considered anomalous;[8] it is likely that the smallness of the separation is related to the high stability of the CO molecule; in the unstable $He_2$ molecule, especially for the more excited states (see below, Table I), the separations between $F_A$ and $F_B$ terms become very large.

The fourth positive bands of CO are without doubt due to a ${}^1S-{}^1P$ transition, as concluded by Birge (cf. I, Fig. 1); the structure of these bands has not been investigated in detail, but so far as it is known, seems to be in agreement with expectation.

The infra-red CO absorption bands should involve ${}^1S$ states only, since the normal state of CO is ${}^1S$ (cf. I, Fig. 1 and p.), and should therefore have the same structure as the infra-red HCl absorption bands.

AlH *Bands.*[7] A system of bands due[9] to AlH has recently been investigated by Mörikofer[10] and by Eriksson and Hulthén.[11] As analyzed by the latter investigators, the bands all have exactly the same structure as the Ångstrom CO bands, except for the missing lines, which agree

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[7] Since $j_s=1$ for ${}^3P_1$ atomic states, it is possible that $\sigma=1$, $\rho=0$ holds for ${}^3P_1$ as well as for ${}^1P$ molecular states, so that ${}^1S-{}^3P_1$ and ${}^3P_1-{}^1S$ transitions might give the same band-structure (including missing lines) as ${}^1S-{}^1P$ and ${}^1P-{}^1S$ transitions,—hence that the CO, AlH, and $He_2$ bands might correspond to transitions of the former rather than of the latter types. But the suggested identity of structure seems doubtful; or if it did exist, it is likely that ${}^1S-{}^3P_1$ combinations would be accompanied by ${}^1S-{}^3P_0$ (possibly also ${}^1S-{}^3P_2$) combinations which would betray them. In the cases of CO (cf. I, Fig. 1 discussion and ref. 38) and $He_2$ (cf. ref. 21 below), there is furthermore definite evidence against the presence of ${}^3P$ states for the bands here discussed.

[8] Dr. E. Hulthén has been so kind as to inform the writer that the $Q$ branches finally begin to show slight combination defects for high values of $j$, thus showing that $F_A''$ and $F_B''$ are really distinct as expected.

[9] That the bands are due to AlH is sufficiently well shown by the experimental conditions (Al arc in $H_2$; also in absorption, in Al vapor plus $H_2$, according to Hulthén and Zumstein, Phys. Rev. **28,** 23 (1926)), and by the small moment of inertia disclosed by their analysis.

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

[11] G. Eriksson and E. Hulthén, Zeits. f. Physik **34,** 775 (1925).

perfectly[12] with Fig. 1*a* ($^1S-{}^1P$ transition), and except for the fact that the $Q$ branches show apparent combination defects indicating that $F_A' \neq F_B'$.[13] The difference between $F_A'$ and $F_B'$ is apparently chiefly in the $B$ values, since an approximate evaluation of the $F$'s from Eriksson and Hulthén's data, assuming Eq. (1*a*), gives, for the band involving vibrational states having $n'=0$ and $n''=0$:

$$F_A'=5.935(j^2-1)+\cdots;\ F_B'=6.00(j^2-1)+\cdots;\ F''=6.29j^2+\cdots \quad (4)$$

*The* $\mathrm{He}_2$ *Bands.*[7] In all the $\mathrm{He}_2$ bands,[14,15,16] the $T$ values are apparently quarter-integral, while $\Delta T$ has the apparent values, $-\frac{1}{2}$, 0, and $+\frac{1}{2}$, for $P$, $Q$, and $R$ branches. But on this basis, the branches which occur appear to be determined by arbitrary and mysterious selection principles. Besides this, there are missing in the λ5733 band two lines, $P'(2)$ and $Q_1(2)$ in Kratzer's numeration, whose absence is not accounted for.

An important clue to the understanding of these bands is the phenomenon of alternating intensities in band lines. This seems to be an exclusive characteristic of molecules composed of two like atoms.[17] Such alternating intensities occur in the second positive $\mathrm{N}_2$, the $\mathrm{N}_2^+$, in certain $\mathrm{H}_2$, and doubtless in other bands.[18] In the Swan (probably $\mathrm{C}_2$) bands, there are three $R$ branches, in each of which, however, alternate lines are slightly displaced, so that each branch must be divided[19] into two series, of doubled spacing. Similar statements hold for the $P$ branches ($Q$ branches have not been observed). In explanation, Heurlinger suggested[19] that each individual series may be thought of as consisting of an alternation of strong and vanishingly weak lines, so placed with respect

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[12] According to Mörikofer, a number of additional lines are present in some of the bands, corresponding to smaller values of $j$ (in some cases negative!) than those noted by Eriksson and Hulthén; but for the most part these are discontinuously weaker than preceding members of the series. Eriksson and Hulthén state that each branch always begins with a strong line, and on the whole it seems legitimate to leave out of account the additional lines noted by Mörikofer.

[13] Except for the missing lines, which indicate a $^1P$ *initial* state, it might be the final instead of the initial states which are double,—as indeed Eriksson and Hulthén supposed.

[14] W. E. Curtis, Proc. Roy. Soc. **101,** 38 (1922): λ5733, 6400 and 4546 bands.

[15] "Series Bands," W. E. Curtis, Proc. Roy. Soc. **103,** 315 (1923); W. E. Curtis and R. G. Long, Proc. Roy. Soc. **108,** 513 (1925). In these bands, combination relations do not exist between the $Q$ branches and the $P$ and $R$ branches (the usual relations exist between the $P$ and $R$ branches). Curtis and Long, however, assume that all three branches are associated with a *common set* of *final* rotational states; this assumption has been adopted here.

[16] A. Kratzer, Zeits. f. Physik **16,** 353 (1923).

[17] Cf. R. Mecke, Zeits. f. Physik **31,** 709 (1925).

[18] Cf. R. Mecke, Phys. Zeits. **25,** 1 (1924); Zeits. f. Physik **28,** 269 (1924).

[19] T. Heurlinger, Dissertation Lund, pp. 46–47 and 52–53 (1918).

to those of the companion series that the strong lines of the one series alternate with those of the other to make the almost-continuous composite series which corresponds to an observed branch (this will be made clearer by an examination of one of the series (of doublets) for the case

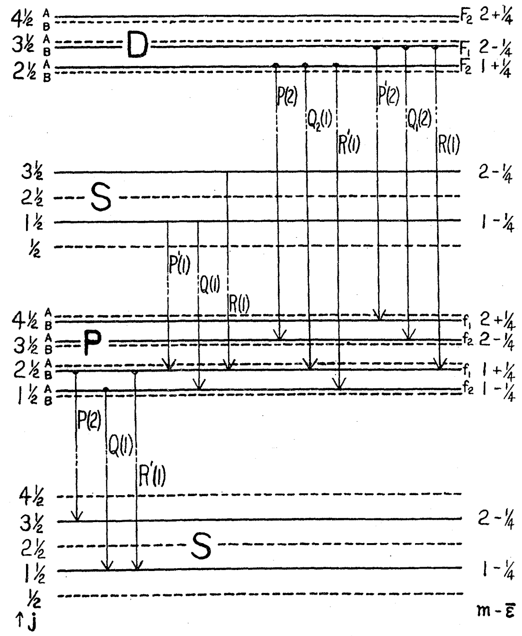

Fig. 2. Rotational energy level schemes for $^1S$, $^1P$ and $^1D$ electronic states in $He_2$, and rotational transitions corresponding to first observed line of each branch (cf. description of Fig. 1) for $^1S-{}^1P$, $^1P-{}^1S$ and $^1P-{}^1D$ combinations. The spacing of the rotational levels is *not to scale*.

The full lines represent levels between which combinations have actually been observed, while the dashed lines correspond to hypothetical intermediate levels whose suppression is probably somehow related to the symmetry of the molecule (cf. refs. 17, 19 and 20). The complete absence of levels having $j=\frac{1}{2}$ in the case of $P$ states, and of levels having $j=\frac{1}{2}$ or $1\frac{1}{2}$ in $D$ states, is ascribed to the presence of a $\sigma$ ($\sigma=1$ for $P$ states, and $\sigma=2$ for $D$ states), and is perhaps the strongest argument from the band structure for the designations $P$ and $D$. The missing lines, and the first lines which are present in each branch, are determined by both these types of missing levels jointly.

At the left of the figure are the $j$ values as here assigned, and the classification of the rotational levels as $A$ or $B$ (for $^1S$ states all the levels are classed as $B$ levels). At the right, for convenience of comparison, are Kratzer's designations for the two observed classes of rotational levels in $P$ and $D$ states, together with his assignment of $m$ and $\bar{\rho}$ values. (In the figure, was $\bar{\epsilon}$ inadvertently used instead of $\bar{\rho}$). The designations given for the first observed lines of each branch are in the notation and numbering of Kratzer and Curtis (the *number* in each case is merely the value of Kratzer's $m''$).

The suppressed levels can be summarized as follows: $B$ levels, $\frac{1}{2}$, $2\frac{1}{2}$, $4\frac{1}{2}$, $\cdots$ for $S$ states, $1\frac{1}{2}$, $3\frac{1}{2}$, $5\frac{1}{2}$, $\cdots$ for $P$ states, and $2\frac{1}{2}$, $4\frac{1}{2}$, $6\frac{1}{2}$, $\cdots$ for $D$ states; $A$ levels, $2\frac{1}{2}$, $4\frac{1}{2}$, $6\frac{1}{2}$, $\cdots$ for $P$ states, $3\frac{1}{2}$, $5\frac{1}{2}$, $\cdots$ for $D$ states.

marked $^1P-^1D$ in Fig. 3 below). If the alternate weak members in each individual series were *not vanishingly* weak, each branch would consist of narrow doublets, of which alternately the high- and the low-frequency component would be the more intense. Exactly this condition is observed in the second positive nitrogen bands, whose structure is identical[19] with that of the Swan bands if Heurlinger's suggestion of alternate missing lines is adopted for the latter.—A suggestion in regard to the cause of such alternating intensities has been made by Slater.[20] The problem has been considered recently by Van Vleck (Phys. Rev., Nov., 1926).

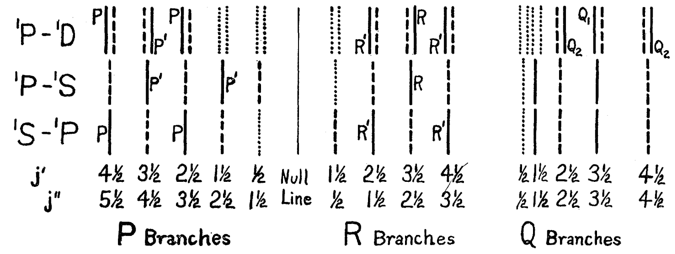

Fig. 3. Diagrammatic representation of arrangement of band lines for the three known types of $He_2$ bands. To avoid confusion the $Q$ branches are drawn separately from the $P$ and $R$ branches. For simplicity the latter are drawn as if given by equations of the form $\nu = A \pm Bj''$; actually there should in general be a slight discontinuity at the null line, corresponding to a small difference in the $A$ values for the $P$ and $R$ branches (cf. Eq. (5) of *I*); and of course there should be terms in $j''^2, j''^3$, etc., in the $\nu$ expression.

In the diagram the full lines represent observed band lines, the dashed lines correspond to "alternate missing lines," while the dotted lines indicate "central missing lines," i.e., band lines which are missing due to the condition that $j$ cannot be less than $\sigma$. The occurrence of only three branches for $^1S-^1P$ and $^1P-^1S$ transitions, but six for $^1P-^1D$ transitions, is due to the singleness of the $^1S$ rotational states, as explained in the text.

If the dashed lines in Fig. 3 be converted into full lines, the diagram becomes identical with that for *ordinary* $^1S-^1P$, $^1P-^1S$, and $^1P-^1D$ transitions, as in AlH, CO, etc.

Mecke has pointed out[21] that the peculiarities of the $He_2$ bands largely disappear if one assumes alternate lines to be missing in each branch (as in Heurlinger's interpretation of the Swan bands). Applying this suggestion,[22] by assuming suitable sets of *alternate suppressed rotational*

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[20] J. C. Slater, Nature **117**, 555, April 17 (1926).

[21] R. Mecke, Phys. Zeit. **26**, 227 (1925).

[22] Adopting a suggestion rejected by Mecke,[17,18] Dieke has proposed the subdivision of each alternating series in $N_2^+$ into two series composed respectively of the strong and of the weak lines (G.H. Dieke, Zeits. f. Physik **31**, 326 (1925)). This, however, gratuitously introduces[17] into the interpretation of the $N_2^+$ bands the peculiarities of the $He_2$ bands, and is open to other objections, e.g., the $B$ values are four times as large as according to the other interpretation, and much larger than for related molecules such as CN and CO. This change in the values of $B$ and other coefficients in the expression for $F(j)$ permit a critical test, however: as Birge has shown (R. T. Birge, Nature **116**, 783 (1925)), the experimental $\omega_0$ values agree with the theoretical relation (cf. below,

*energy levels*, it becomes evident that the "series bands"[15] are of exactly the same type (three branches, combination defects in *P–Q–R* combinations,[15] etc.) as the $^1S-{}^1P$ AlH bands, while the bands λ4546 and λ6400 fall at once under the $^1P-{}^1S$ type. The band λ5733, which has the same final state as λ4546 and λ6400,[16] differs from all the other known $He_2$ bands in having six branches (and in being shaded toward the violet), and also has more missing lines per branch than any of the other $He_2$ bands. The missing lines, hitherto not explained, are on the new basis exactly those to be expected for a $^1P-{}^1D$ transition ($\sigma'=2$, $\sigma''=1$). This band now constitutes the typical example of the general case of a combination of two $\sigma$-type terms in agreement with Eq. (2), and furnishes in fact the experimental basis for Eq. (2).[5] It also shows definitely, by elimination, that it is the $^1S$ state which is responsible for the fewness of branches and other peculiarities of $^1S-{}^1P$ and $^1P-{}^1S$ combinations.

The relations stated in the preceding paragraph will become clear by a study of Figs. 2 and 3.

Starting with the assignment of electronic term designations just arrived at, strong evidence for their correctness was given in a previous paper,[23] to which reference should be made, on the ground of series relations of the electronic terms (supplementing the work of Fowler and of Curtis and Long); this evidence may now fairly be cited on its own merits as giving support to the interpretations here given of the *structure* of the $He_2$ bands. There is, furthermore, direct evidence (see below) in favor of the scheme of rotational levels given in Fig. 2, and in addition, the new interpretation leads to more reasonable $B$ and $\omega_0$ values than the old (cf. refs. 23 and 23a, also Table I, p. 1215); all this is in addition to the satisfactory explanation of the band structure.

In the above-mentioned paper,[23] it was shown that the electronic terms in the "main series"[15] and related bands (λλ6400, 4546, 5733) parallel the "doublet" (presumably triplet) terms of the He atom, while the electronic terms of the "second series"[15] bands parallel the singlet terms

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p. 1214) $\omega_0=\sqrt{4B^3/\beta}$ only if the alternate strong and weak members of each otherwise continuous series are assumed, contrary to Dieke's interpretation, to belong physically to a single series. Hence the assumption of the extreme case of alternating intensity, i.e., alternate missing lines, in the Swan bands and in the $He_2$ bands, cannot be considered a radical one.

[23] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 158 (1926). The writer wishes to express here his regret at having failed to notice until recently a paper by Y. Takahashi (Jap. J. of Physics **2**, 103 (1923)) in which electronic term designations for the $He_2$ bands were proposed, in part similar to those arrived at later by the writer. Attention may also be called to Curtis and Long's discussion of the nature of the terms and of the emitting molecule (l.c., ref. 15, pp. 533–38).

[23a] R. Mecke, Zeits. f. Physik **32**, 823 (1925).

of the atom. In explanation it was suggested that the "main series" is emitted by molecules composed in their least excited state of two He atoms each in the metastable 2 $^3S$ state, and the less prominent "second series" by more loosely bound molecules composed of two atoms each in the metastable 2 $^1S$ state. In the former case (2 $^3S$, 2 $^3S$), the resultant molecular $^1S$ state ($j_e=0$) must evidently arise from an interaction and mutual neutralization of the $j_e$'s of the two atoms ($j_e=1$ for each), while in the latter case (2 $^1S$, 2 $^1S$), with $j_e=0$ for each atom, no interaction is needed to give the $^1S$ molecular state.[24] The conceivable case (2 $^1S$, 2 $^3S$) seems not to be present in bands now known, while the cases (1 $^1S$, 2 $^3S$) and (1 $^1S$, 2 $^1S$) may fairly safely be left out of consideration in view of the inertness of the normal (1 $^1S$) state of the He atom. The known *excited* electronic states of the $He_2$ molecule presumably correspond to the excitation of an electron (above the 2 $S$ state) in one atom only, to electronic states belonging to the same system (triplet for the main series, singlet for the second series) as for the corresponding least excited state of the molecule. This accounts for the marked resemblance of the molecular *term values* to those of corresponding atomic terms. But in spite of this resemblance the *multiplicity* is completely changed, in the case of the molecular forms composed of two triplet atoms, by the interaction of the two atoms.

The direct evidence for the alternate missing level scheme of Fig. 2 is as follows. In Fig. 2 the arrangement of the missing levels differs for $^1S$, $^1P$, and $^1D$ states; but for *all the states of each type* the same characteristic arrangement must exist. This is shown for $^1S$ states by the identical structure of the two bands λ6400 and λ4546 ($2P-3S$ and $2P-4S$),[23] and for $^1P$ states by the identical structure of all members of the series $2S-mP$,—for both "main" and "second" series. From the scheme of levels in Fig. 2, it can then readily be seen that $P$ and $R$ branches should be impossible in $^1S-{}^1S$ transitions, while $Q$ branches are not to be expected, since they are absent in known $^1S-{}^1S$ transitions (CuH, etc.). Similarly, $P$, $Q$, and $R$ branches should all be impossible (assuming Eq. 2) in $^1P-{}^1P$ (and $^1D-{}^1D$) transitions, as can be seen from the figure.

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[24] That the known molecular electronic states are all of a singlet type is fairly satisfactorily shown by the comparative simplicity of the band structures; if any of the bands involved triplet terms, a corresponding multiple $\nu^e$ would be expected, at least in the case of λ6400, 4546 and 5733, whose common final $2P$ state, if it were $^3P$ rather than $^1P$, should probably be resolved, since in the atom the 2 $^3P$ ($2P$ "doublet") state shows an appreciable separation into (apparently two) components; or if an electronic fine structure were present but unresolved, it should still make itself felt by the occurrence of more than one value of $\sigma$, with a corresponding change (reduction) in the number of missing lines,—and also perhaps in other ways.

There is no reason to expect these transitions to be barred as in line spectra by a selection principle, since intense $S-S$ and $P-P$ combinations are known for other molecules. It then seems very significant that no $He_2$ bands corresponding to either ${}^1S-{}^1S$ or ${}^1P-{}^1P$ transitions are known. Dr. Curtis has recently re-examined his plates and has been so kind as to inform the writer that he finds no evidence of any of the combinations $2S-3S$, $2S-4S$, $2P-3P$, $2P-4P$, although if present, their location is such that they should all have been rather easily detected. This result gives strong support to the missing level scheme of Fig. 2.[25]

The new interpretation of the $He_2$ bands here proposed requires a re-interpretation of $\Delta F$ values and a corresponding re-evaluation of coefficients. In general for any band spectrum, the $\Delta F$'s, when correctly evaluated by means of combination relations (cf. I, p. 490), are empirical quantities which are unalterable by any change of theory (other than a loss of faith in the combination principle). The determination of $F$'s from $\Delta F$'s depends, however, on additional theoretical considerations. In the present case, the change in the theory introduced is fortunately of such a character that the new $F$'s can be obtained from the old $F$'s of Kratzer and Curtis and Long by a simple transformation, without the necessity of going back to the original $\Delta F$ values. (This can be seen by an examination of the definition of $\Delta F$ in relation to the following equations.)

For the $F$ values, Kratzer[16] assumed in effect the following form; in this equation $M=m-\bar{\rho}$, and $M^*=m-\bar{\theta}$ (the notation here used differs from Kratzer's):

$$\bar{F}(M)=\bar{B}M^2-\bar{\beta}M^{*4}+\cdots \tag{5}$$

In Eq. (5) Kratzer *assumed* $m$ (not $M$) to be integral, and then found $\bar{\rho}$ to have approximately the values $+\frac{1}{4}$ and $-\frac{1}{4}$; $\bar{\theta}$ is a quantity of the same sign as $\bar{\rho}$ but differing considerably from $\bar{\rho}$, according to Kratzer's analysis, in numerical value.[26]

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[25] Except for this evidence, the observed facts could be accounted for in either of two other ways which represent modifications of the scheme of alternate missing levels given in Fig. 2: it can be assumed (1) that *all* the rotational levels are present for the $D$ states, but that alternate levels are missing as in Fig. 2 for the $S$ and $P$ states (an additional possibility scarcely worth mentioning is that the $S$ levels, *except* $j=\frac{1}{2}$, are all present, either instead of, or in addition to, the full set of $D$ levels); or (2) that all the rotational levels are present for $P$ states, but that alternate levels are missing as in Fig. 2 for $S$ and $D$ states. Neither of these is very plausible, and at least the second of the two possibilities (as also the possibility that all or all but one of the rotational levels are present for $S$ states) seems to be definitely negatived by the evidence given in the text.

[26] It should be remarked that $m$ as used by Kratzer was *intended* by him to be identical in significance with $j$ as here used, although in the revised interpretation of the $He_2$ bands here proposed this is not the case.

The assumption of alternate missing lines and rotational levels means that the succession of observed $M$ values, $M_0$, $M_0+1$, $M_0+2$, $\cdots$, is to be interpreted as corresponding to alternate members $2M_0$, $2M_0+2$, $2M_0+4$, $\cdots$, of a succession of values $(2M_0-1)$, $2M_0$, $2M_0+1$, $\cdots$, the levels corresponding to $(2M_0-1)$, $2M_0+1$, $2M_0+3$, $\cdots$, being assumed to be suppressed (at least in respect to the emission of radiation). Since the $M$'s always have approximately quarter-integral values, the ($2M$'s) all have approximately half-integral values; according to the present interpretation, $2M$ is to be identified with $T$. But the $j$ *values* should be half-integral for $He_2$, since it is an even molecule (cf. I, postulate *III*). Since $T$, which is necessarily equal to $j-\rho$ if the rotational terms are essentially, as we assume, of the Kramers and Pauli form, is approximately half-integral, we conclude that $T\sim j$, and $\rho\sim 0$, the usual small deviations of $T$ from exact half-integral values being ascribed to small "secondary" $\rho$'s. The resulting interpretations are then in harmony with those already adopted for the CO and AlH bands.

In terms of $T$, Eq. (5) can now be rewritten

$$\bar{F}(T)=(\bar{B}/4)T^2-(\bar{\beta}/16)T^{*4}+\cdots \tag{6}$$

Then, putting $\bar{\beta}/16=\beta$ and $(\bar{B}/4)-2\beta\sigma^2=B$, and neglecting the difference between $T$ and $T^*$[27], and adding the experimentally not directly detectable small terms $-B\sigma^2$ and $-\beta\sigma^4$, Eq. (6) can be reduced to the following form, which is merely Eq. (3) with the addition of the next higher power term as obtained by Kemble:[28]

$$F(j)=B[(j-\rho)^2-\sigma^2]-\beta[(j-\rho)^2-\sigma^2]^2+\cdots \tag{7}$$

Here $\rho$ is related to $\bar{\rho}$ by the equation $\rho=2\bar{\rho}\pm\frac{1}{2}$, the upper sign for $\bar{\rho}$ negative, the lower for $\bar{\rho}$ positive. The values of $B$, $\beta$, and $\rho$ for each electronic state can now be obtained by simple calculation from the values given by Kratzer and Curtis and Long.[27] The vibration frequencies also, although not directly observed, can probably be approximately calculated by means of the theoretical relation[29] $\omega_0=\sqrt{4B^3/\beta}$. The values of $\omega_0$

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[27] Strictly, of course, the constants (especially $\beta$) should be re-evaluated from the original data, but this will not be attempted here.

[28] In the forthcoming National Research Council Report on Molecular Spectra, Kemble shows that the complete Kramers and Pauli term (Eq. (8) of *I*) has the form $F(j)=Bm^2-\beta m^4+\cdots$, with $m=\sqrt{j^2-\sigma^2}-\rho$ as in Eq. (8) of *I*. The corresponding completed form of Eq. (3) is Eq. (7).

[29] Cf. A. Kratzer, Ann. der Physik **71**, 80 (1923). The relation is strictly applicable only when $n=0$ (E. C. Kemble, J.O.S.A. **12**, 1 (1926); $\beta$ as used here is Kemble's $D$); fortunately the known $He_2$ bands probably all have $n'$ and $n''$ equal to zero.

previously calculated by Kratzer and Curtis and Long must be approximately halved, since $\sqrt{4B^3/\beta} \sim \frac{1}{2}(\sqrt{4\overline{B}^3/\bar{\beta}})$.

The $He_2$ bands now illustrate well the phenomenon of rotational doubling for $\sigma$-type terms. Accordnig to Curtis and Long's analysis of the bands of the "main series," the $\rho$ values for the $3P$ electronic state are small or negligible, and the $\nu^e$ and $B$ values are practically the same for $F_A$ and $F_B$ states; but for more and more excited $P$ states, a progressively increasing separation between the $F_A$ and $F_B$ states develops, so that for the most excited $P$ states the $\rho_B$ values are large, and the $B_B$ values are much less than for the $3P$ state, while the $\rho_A$ values remain small, and $B_A$ falls only slightly with increasing electronic excitation. This striking difference in behavior of $F_A$ and $F_B$ terms should be of assistance in determining the nature of the $\sigma$ type of rotational doubling.

TABLE I

*Constants of molecular helium in various electronic states*

| El. State[23] | $B_A$ | $B_B$ | $\rho_A$ | $\rho_B$ | $\beta_A \times 10^4$ | $\beta_B \times 10^4$ | $\omega_0$ | $r_0$(A.U.) $A$ | $r_0$(A.U.) $B$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | A. Main series and related bands | | | | | |
| $2S$ | 7.589 | | .001 | | 5.51 | | 1780 | 1.050 | |
| †$3S$ | 7.21 | | 0 | | .... | | .... | 1.079 | |
| †$4S$ | 7.13 | | 0 | | .... | | .... | 1.084 | |
| †$2P$ | 7.320 | 7.320 | −.004 | .004 | 5.08 | 5.08 | 1760 | 1.070 | |
| $3P$ | 7.175 | 7.102 | .003 | 0 | 5.17 | 5.01 | 1690 | 1.081 | 1.086 |
| $4P$ | 7.140 | 6.966 | .005 | 0 | 5.32 | 4.48 | 1700 | 1.084 | 1.098 |
| $5P$ | 7.130 | 6.944 | .013? | .066? | 5.33 | 4.65 | 1680 | 1.084 | 1.100 |
| $6P$ | 7.116 | 6.722 | .004 | .042 | 5.32 | 4.31 | 1670 | 1.085 | 1.117 |
| $7P$ | 7.117 | 6.637 | .006 | .092 | 5.45 | .... | | 1.085 | 1.124 |
| $8P$ | 7.111 | 6.646 | .005 | .222 | 5.37 | .... | | 1.086 | 1.122 |
| $9P$ | 7.14 | ..... | .01 | .... | 8.5 | | | 1.084 | |
| $10P$ | 7.18 | ..... | .02 | .... | 11.3 | | | 1.081 | |
| †$3D$ | 7.555 | 7.555 | −.003 | .003 | 7.37 | 7.37 | 1530 | 1.052 | |
| | | | | B. Second series. | | | | | |
| $2S$ | 7.65 | | .00 | | | | | 1.047 | |
| $3P$ | 7.17 | 7.12 | .02 | .02 | | | | 1.08 | 1.08 |
| $4P$ | 7.11 | 6.97 | .00 | −.02 | | | | 1.09 | 1.10 |
| $5P$ | 7.17 | 6.74* | .06* | −.14* | | | | 1.08 | 1.12 |
| $6P$ | 7.18 | 6.60* | .05* | −.19* | | | | 1.08 | 1.13 |

*Notes*: (1) the values of $\omega_0$ (the vibration frequency) are average values calculated from both $F_A$ and $F_B$ terms. (2) $r_0$ is the internuclear distance, calculated from $B$. (3) The data for the states marked † are from Kratzer's analysis, the remaining data from Curtis and Long's work. On account of certain differences in the method of analysis, the two sets of data are not strictly comparable. In particular, the opposite signs and equal magnitudes of $\rho_A$ and $\rho_B$, and the exact equalities of $B_A$ and $B_B$, and of $\beta_A$ and $\beta_B$, for the $2S$ and $3D$ terms, are not significant, since they were in effect *assumed* by Kratzer as a part of the theoretical preliminaries to the determination of constants to fit the observed data. Also, (even the mean) $\beta$ and $\omega_0$ values of Kratzer and of Curtis and Long are not exactly comparable, since Kratzer assumed $M$ and $M^*$ of Eq. (5) to be distinct, while Curtis and Long assumed them identical. (4) It is not certain that the negative $\rho_B$ values for the $P$ terms of the second series are significant, since no great accuracy is claimed for the analysis (this is especially so in the cases marked*)

The $\rho$, $B$, and $\omega_0$ values for all known electronic states of $He_2$ are given in Table I; these values are essentially results of the work of Curtis and Long and of Kratzer, having been subjected here, without re-examination of the original data, only to the simple transformations indicated in connection with Eqs. (6) and (7). For the $\nu^e$ values, reference should be made to Curtis and Long's and Kratzer's papers (the values given by these authors should of course be slightly altered, essentially by the amount of the appropriate $B\sigma^2$ terms).

*Alkali metal bands.* All the alkali metals show band absorption spectra which are commonly attributed to diatomic molecules $Na_2$, $K_2$, etc. This is justified by the close spacing of the band lines,[30,31] the very low vibration frequencies,[32] and especially by the fact that similar but new and characteristic spectra (e.g. the NaK bands) appear in mixed alkali metal vapors.[31,33]

No satisfactory analysis of any of these bands, making use of combination relations, has been carried through, although Smith[31] has arranged a number of the $Na_2$, NaK, and $K_2$ bands, mostly in three branches ($P$, $Q$, and $R$). But from R. W. Wood's work on the "resonance spectra" excited in sodium vapor by monochromatic light, it seems fairly clear, as will be shown, that the yellow and green $Na_2$ bands[32] are due to a transition $^1S-{}^1P$ like the AlH bands.

Let us assume for the time being the correctness of this characterization. Sodium molecules in a variety of vibrational and rotational states of the $^1S$ electronic state should then be present in the heated absorption tube (temperature about 400°C in Wood's experiments). If the vapor is illuminated with monochromatic light of suitable wave-length, molecules in one of these states will be enabled to go to a particular vibrational and rotational state belonging to the $^1P$ excited electronic state. If the

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[30] R. W. Wood, Physical Optics, pp. 571-79, 1919 ed.

[31] H. G. Smith, Proc. Roy. Soc. **106,** 400 (1924).

[32] An inspection of Wood's Fig. 350 (ref. 30, p. 574) shows that the green and yellow $Na_2$ absorption bands together form a typical band-system. This can easily be seen by comparison with e.g., the writer's photograph (Phys. Rev. **26,** 1, (1925)) of the green CuI bands ($A$ bands). The arrangement and vibrational intensity distribution in the $Na_2$ bands are closely similar to those in the $A$ bands of CuI. From Wood's figure it can also be seen that $n''$ reaches values as high as 15, while $n'$ also reaches fairly high values.—The vibration frequency $\omega_0''$ for the final state can be obtained approximately from Wood's $Na_2$ resonance series, being roughly equal (in wave-number units) to the spacing of the two highest-frequency members of any such series. This procedure yields $\omega_0''\sim 150$. From the structure of the absorption spectrum (cf. Wood's Fig. 350), it is then possible to deduce $\omega_0'\sim 127$.

[33] S. Barratt, Proc. Roy. Soc. **105A,** 221 (1924); F. H. Newman, Phil. Mag. **48,** 159 (1924); P. Pringsheim, Zeits. f. Physik **38,** 161 (1926), and refs. there cited.

absorbed light should correspond to a $Q$ branch line, the molecule goes to an $F_A$ rotational state, if to either a $P$ or an $R$ line, it goes to an $F_B$ rotational state (cf. Fig. 1*a*). From an $F_B$ excited state the molecule can return by either a $P$ or an $R$ transition ($\Delta j=-1$ or $+1$) to any vibrational level of the normal electronic state of the molecule; this process should give rise to a typical series of "resonance doublets" (as in the $I_2$ bands[34]), the different doublets in the series corresponding to different final vibrational states of the molecule. But from an $F_A$ rotational state the molecule can return only by a $Q$ transition ($\Delta j=0$), so that here the resonance series should consist of a set of single lines.

For a ${}^1P-{}^1S$ transition, on the other hand, the resonance series should all consist of *triplets* ($P$, $Q$, $R$), as can be seen by a study of Fig. 1*b*; the same is true of a ${}^1P-{}^1D$ or ${}^1D-{}^1P$ transition, as can be seen by consideration of Eq. (2). For a ${}^1S-{}^1S$ transition, *doublet* series *alone* are to be expected, since only $P$ and $R$ transitions occur in such bands; the resonance spectrum of $I_2$, as investigated by Wood and interpreted by Lenz,[34] appears to be of this type.[35] In the case of a ${}^1P-{}^1P$ (or ${}^1D-{}^1D$) transition, resonance triplets are to be expected (cf. Eq. 2), but should appear in practice as doublets, since for such transitions the $Q$ branch should be much weaker and shorter than the $P$ and $R$ branches (as is shown by an application of the correspondence principle, discussed in III of this series). The $I_2$ bands might be of such a type,[35] if it were not that $I_2$ vapor is probably (by analogy with $Cl_2$ gas) diamagnetic; this indicates a ${}^1S$ normal state (cf. I, p. 504), and so seems to rule out ${}^1P-{}^1P$ here in favor of ${}^1S-{}^1S$.

The work of Wood and Hackett on the green $Na_2$ absorption bands shows[30] that some absorbed wave-lengths (e.g. Cd λ4800) give rise to resonance series composed of single lines, others (e.g. Cd λ5086) to series composed of doublets. Since this behavior agrees with that predicted

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[34] W. Lenz, Phys. Zeits. **21**, 691 (1920). Cf. A. Sommerfeld, Atombau und Spektrallinien, 4th Ed., pp. 725–26, for brief discussion. Cf. also E. C. Kemble and E. E. Witmer, Phys. Rev. **28**, 633 (1926).

[35] Since $I_2$ and $Na_2$ are each composed of two like atoms, the suppression of alternate rotational levels (partial as in $N_2$ and $N_2^+$, or complete as in $He_2$) is likely, for some at least of the electronic states of these molecules. A study of Fig. 2 will show, however, that the nature (doublets, triplets, or singlets and doublets) of the resonance series to be expected, for any type of electronic transition, would be unaffected by this circumstance (except for the one special case of $j'=1\frac{1}{2}$, for a ${}^1P-{}^1S$ transition). Absorption and resonance would, however, be completely suppressed for ${}^1S-{}^1S$, ${}^1P-{}^1P$, or ${}^1D-{}^1D$ combinations (cf. above, p. 1213) in case the suppression of alternate rotational levels is complete in *both* upper and lower electronic states; the latter condition therefore probably does not exist in the case of $I_2$.

for a $^1S-^1P$ transition and for no other,[35,36] it is probable that the $Na_2$ band-system[32] in this region is of this type. It is likely that the red $Na_2$ system, as well as other systems further in the ultra-violet, are of the same type. If so, the various excited $^1P$ states are probably due to a rather loose union of a normal ($3\,^2S$) and an excited ($m\,^2P$) Na atom, and the normal $^1S$ molecular state to a similar union of two normal atoms.[37] The red bands may be $3\,^1S-3\,^1P$ (corresponding to the $D$ lines of the Na atom, but, as expected, lacking the doublet character of the latter, of which there seems to be no evidence in any of the $Na_2$ bands), and the yellow and green bands $3\,^1S-4\,^1P$. So far as they are known, the NaK, $K_2$, and other alkali metal absorption bands are all closely analogous to the $Na_2$ bands, and so presumably correspond to the same type of electronic transition.[36]

## B. SPECTRA OF MOLECULES WITH AN ODD NUMBER OF ELECTRONS

*$^2S-^2P$ and $^2P-^2S$ combinations.* In even molecules, as we have seen, $j_e=\sigma=1$ for $^1P$ states, while $j_e=0$ for $^1S$ states, and for both states $T=j=$half-integral. As a result, the band structure is comparatively simple in $^1P-^1S$ and $^1S-^1P$ transitions. For odd molecules, however, the band structure is necessarily more complicated in $P$–$S$ transitions, according to the conclusions and postulates of I: in $^2S$ states, $j_e=\rho=\pm\frac{1}{2}$, while for $^2P$ states $j_e=\sigma$ ($\sigma=\frac{1}{2}$ for $^2P_1$ and $1\frac{1}{2}$ for $^2P_2$ states), so that $T=j\mp\frac{1}{2}=$half-integral for $^2S$ states but $T=j=$integral for $^2P$ states.

The only examples of $^2S-^2P$ transitions whose structure is known in detail are the ZnH, CdH, and HgH bands. The interpretation of these bands in agreement with the postulates of I (modifying Kratzer's previous interpretation) has been discussed in an earlier paper,[2] to which reference should be made. Due presumably to the fact that they involve both $\rho$-type and $\sigma$-type terms, the observed branches appear to be determined in a different way than for cases involving only $\sigma$-type terms as in Eqs. (1) above. Briefly, the behavior of the initial $\sigma$-type states here is such that the observed rotational doubling is more appropriately classified, like that of the final $\rho$-type states, in accordance with the $\rho$-type notation ($F_1$, $F_2$) than with the $F_A$, $F_B$ notation of Eqs. (1) and (2). The $Q$ branches, however, show crossing over as in Eqs. (1) and (2). Further details are given in ref. 2.

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[36] It is, however, not out of the question that some other transition involving electronic terms of triplet or higher multiplicity might show the same behavior as $^1S-^1P$ (cf. ref. 7).—The occurrence of triplet states for alkali metal molecules is indeed likely, but there is no obvious evidence of it as yet.

[37] Cf. R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 338 (1926), for further discussion. Also cf. J. Franck, Trans, Faraday Soc., 1925.

For $^2S-{}^2P_1$ and for $^2S-{}^2P_2$ transitions, the following equations hold (neglecting higher power terms), as is shown by the ZnH, CdH, and HgH bands:

$$\begin{aligned} R_1(j-1),R_2(j-1)&=\nu^0+F_1'(j),F_2'(j)-B''(j-1\mp\epsilon)^2\\ Q_1(j),Q_2(j)&=\nu^0+F_2'(j),F_1'(j)-B''(j\mp\epsilon)^2\\ P_1(j+1),P_2(j+1)&=\nu^0+F_1'(j),F_2'(j)-B''(j+1\mp\epsilon)^2 \end{aligned}\tag{8A}$$

Letting $\nu'=\nu^0-B''\epsilon^2$, these give on expansion:

$$\begin{aligned} R_1(j-1)&=\nu'+F_1'(j)-B''(1+2\epsilon)+2B''(1+\epsilon)j-B''j^2\\ R_2(j-1)&=\nu'+F_2'(j)-B''(1-2\epsilon)+2B''(1-\epsilon)j-B''j^2\\ Q_1(j)&=\nu'+F_2'(j)\qquad\qquad\qquad +2B''\epsilon j\qquad -B''j^2\\ Q_2(j)&=\nu'+F_1'(j)\qquad\qquad\qquad -2B''\epsilon j\qquad -B''j^2\\ P_1(j+1)&=\nu'+F_1'(j)-B''(1-2\epsilon)-2B''(1-\epsilon)j-B''j^2\\ P_2(j+1)&=\nu'+F_2'(j)-B''(1+2\epsilon)-2B''(1+\epsilon)j-B''j^2 \end{aligned}\tag{8}$$

Approximately, $F_1'(j)=F_2'(j)=B'(j^2-\sigma^2)$, and approximately, $\epsilon=\frac{1}{2}$. In general, these equalities are not exact, and there are six distinct branches, as in ZnH, CdH, and HgH. But in the special case that they *are* exact,[38] a complete coalescence of certain branches should occur. For this case, if $\bar{\nu}^0=\nu^0-B'\sigma^2-B''\epsilon^2(\sigma=\frac{1}{2}$ for a $^2P_1$, or $1\frac{1}{2}$ for a $^2P_2$, electronic state), and $C=B'-B''$, Eqs. (8) reduce to the form:

$$\begin{aligned} R_1(j-1)&=\bar{\nu}^0-2B''+3B''j+Cj^2\\ R_2(j-1)&=Q_1(j)=\bar{\nu}^0+B''j+Cj^2\\ Q_2(j)&=P_1(j+1)=\bar{\nu}^0-B''j+Cj^2\\ P_2(j+1)&=\bar{\nu}^0-2B''-3B''j+Cj^2 \end{aligned}\tag{8B}$$

Thus (cf. I, Eq. 5 and p. 492) the $R_1$ branch is 3/2-$R$-form, the $R_2$ and $Q_1$ branches are semi-$R$-form, the $Q_2$ and $P_1$ branches semi-$P$-form, and the $P_2$ branch 3/2-$P$-form.

So far as can be seen from the obvious structure and the fragmentary detailed evidence now available, the precise state of affairs[38] expressed in Eqs. (8$B$) actually occurs in the red CN, BO$\alpha$, and CO$^+$ comet tail bands (all of which are $^2S-{}^2P$ transitions like ZnH etc., cf. I, Fig. 1). The condition $\epsilon''=$exactly $\frac{1}{2}$ which is necessary for Eqs. (8$B$) is probably met[39]

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[38] The equality $F'(j)=B'(j^2-\sigma^2)$ is of course not necessary, so long as $F'_1=F'_2$; e.g., the presence of a secondary $\rho$ as in Eq. (3) is permissible, provided this $\rho$, and also $B'$, have the same values for $F_1$ and $F_2$.

[39] The red CN bands have the same final state (cf. Fig. 1 of I, discussion) as the violet CN bands. In ref. 13 of I it was stated that Birge has shown that $\epsilon''=$exactly $\frac{1}{2}$ for the latter. This definite statement is unfortunately in error, but the relation in question is nevertheless probable.

(assuming the essential correctness of Kratzer's interpretation of the violet CN bands as discussed in I) in the case of CN, and so by analogy may be expected for BO, $CO^+$, etc. The fulfillment both of this relation and of the necessary exact equality of $F_1'$ and $F_2'$ may be attributed to the relatively high stability of the molecules in question (cf. discussion above under CO), which is in contrast to that of the loosely bound molecules of the ZnH type.

Baldet has concluded[40] that the comet tail bands of $CO^+$ consist of a weak $R$ branch, two strong $Q$ branches, and a weak $P$ branch. This otherwise puzzling result finds obvious explanation in Eqs.(8$B$). Furthermore, Blackburn's work on these bands shows[41] that the two strong branches are related as a $P$ and an $R$ branch, but with $\Delta T$ (previously implicitly assumed[41] to be $\Delta m$ as in bands of the violet CN or CuH type) equal to $\pm\frac{1}{2}$. Also, the analysis shows combination relations between these two strong branches which yield $\Delta_1 F$'s[42] giving $T'$=integral, $T''$=half-integral.[41] All this is exactly what would be expected according to the present interpretation in terms of Eqs. (8$B$).

It should be emphasized that the success of Eqs. (8) in interpreting the structure of the ZnH, CdH and HgH bands is strong direct evidence for the reality of the double sign of $\rho$ (as introduced by Kratzer), with $\epsilon\sim\frac{1}{2}$. Furthermore, the applicability of Eqs. (8$B$) to the red CN bands (assuming that it will be confirmed by a detailed analysis)[42a] will give assurance of the reality of $\rho''=\pm\frac{1}{2}$ for the violet as well as for the red CN bands, since these have a common final electronic state (cf. Fig. 1 of I, discussion). The essential features of Kratzer's interpretation of the violet CN bands should thereby receive a direct justification which is not possible (cf. I, ref. 14) by a consideration of these bands alone.—As already mentioned in I (pp. 500-1), the CH bands, essentially as interpreted by Kratzer, give additional direct evidence for a $\rho$ having the values $\pm\frac{1}{2}$.

For transitions $^2P_{1,2}-{}^2S$, as in the combination bands of BO and $CO^+$ and the third positive NO bands (cf. I, Fig. 1), the predicted branches are easily shown to be of the same general forms as in Eqs. (8), and a similar coalescence, here of the $R_1$ and $Q_2$, and of the $P_2$ and $Q_1$ branches, should take place if $\epsilon'$=exactly $\frac{1}{2}$ and $F_1''=F_2''$. Complete coalescence

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[40] F. Baldet, Compt. Rend. **180**, 820 (1925).

[41] Cf. R. S. Mulliken, Phys. Rev. **26**, 565 (1925).

[42] The combinations can equally well be regarded as between $R_2$ and $Q_2$, or as between $P_1$ and $Q_1$, and so in either case yield $\Delta_1 F$'s (cf. *I*, p. 491), provided of course the necessary conditions (in particular $F_1'=F_2'$) for Eq. (8$B$) are met.

[42a] High dispersion photographs of these bands have been obtained, and their measurement is in progress.

is probably not to be expected, in the examples mentioned; narrow doublets should probably be present. The obvious structure of the bands above mentioned is of the predicted type, but no detailed analysis of any of them has yet been made.

*Other combinations.* For transitions such as $^2P-^2D$, $^2D-^2P$, $^2P-^2P$, etc., Eqs. (2) and (3) may be expected to hold, and the band-structures, except for the missing lines and the occurrence of *integral* $T$ values, should be essentially the same as for $^1P-^1D$, $^1D-^1P$, $^1P-^1P$, etc. Predictions for specific cases are readily made; an example will now be given.

In $^2P_2-^2D_3$ or $^2P_1-^2D_2$ transitions, intense $P$, $Q$, and $R$ branches are to be expected, with each line a doublet. For $^2P_2-^2D_3(\sigma'=2\frac{1}{2}, \sigma''=1\frac{1}{2})$, the $j$ values $(j'\rightarrow j'')$ for the first lines of the various branches should be $R(3\rightarrow 2)$; $Q(3\rightarrow 3)$; $P(3\rightarrow 4)$, there being five missing lines in the otherwise continuous series formed by the $P$ and $R$ branches. For $^2P_1-^2D_2$ $(\sigma'=1\frac{1}{2}, \sigma''=\frac{1}{2})$, the structure should of course be the same, but with only three missing lines in the $P$ and $R$ branches,—$R(2\rightarrow 1)$, $Q(2\rightarrow 2)$, and $P(2\rightarrow 3)$ being the expected first lines.

## C. Summary of Spectrum Interpretations Previously Given

In the following table, the interpretations of individual spectra given in this and the preceding paper are summarized for convenience of reference. In the table, each emitter or spectrum named is typical; additional representatives of each type are given following the table.

### Table II

*Structure types and their interpretation*

| Type | Spectrum | Branches | $T'_{\text{min}}$ | $T''_{\text{min}}$ | Electr. qu. nos. | | | | Electr. transitions |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\rho'$ | $\sigma'$ | $\rho''$ | $\sigma''$ | |
| I | CuH | $P, R$ (2) | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | $^1S-^1S$ |
| IIa | AlH | $P, Q, R$ (3) | $1\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 1 | 0 | 0 | $^1S-^1P$ |
| IIb | Ångstrom CO | $P, Q, R$ (3) | $\frac{1}{2}$ | $1\frac{1}{2}$ | 0 | 0 | 0 | 1 | $^1P-^1S$ |
| III | $He_2\lambda5733$ | $P, Q, R$ (6) | $2\frac{1}{2}$ | $1\frac{1}{2}$ | 0 | 2 | 0 | 1 | $^1P-^1D$ |
| IV | Violet CN | $P, R$ (4) | $\frac{1}{2}$ | $\frac{1}{2}$ | $\pm\frac{1}{2}$ | 0 | $\pm\frac{1}{2}$ | 0 | $^2S-^2S$ |
| Va | ZnH | $P, Q, R$ (6) | 1 | $(\frac{1}{2})$ | 0 | $\frac{1}{2}$ | $\pm\frac{1}{2}$ | 0 | $^2S-^2P_1$ |
| | | $P, Q, R$ (6) | 2 | $(\frac{1}{2})$ | 0 | $1\frac{1}{2}$ | $\pm\frac{1}{2}$ | 0 | $^2S-^2P_2$ |
| Vb | NO 3rd positive (prediction) | $P, Q, R$ (6) | $(\frac{1}{2})$ | 1 | $\pm\frac{1}{2}$ | 0 | 0 | $\frac{1}{2}$ | $^2P_1-^2S$ |
| | | $P, Q, R$ (6) | $(\frac{1}{2})$ | 2 | $\pm\frac{1}{2}$ | 0 | 0 | $1\frac{1}{2}$ | $^2P_2-^2S$ |
| VIIa | CHλ3900 | $P, Q, R$ (6) | $\frac{1}{2}$ | | $\pm\frac{1}{2}$ | 0 | $\pm\frac{1}{2}$(?) | 1(?) | $^1P-^1S$ in C atom(?) |

*Notes for Table II.* (*a*) The $T$ values given are *observed* values (except for $H_2$ and NO 3rd positive bands) *smoothed* to exact integers or half-integers; for the $He_2$ bands, the values given are *twice* the *apparent* values (cf. above). In Type Va the value $\frac{1}{2}$ of $T''_{\text{min.}}$ applies to $F_1$ terms (and corresponds to $j''=1$); for $F_2$ terms the *observed* value of $T''_{\text{min.}}$ in the HgH bands is $1\frac{1}{2}$ (also corresponding to $j''=1$); the absence in these bands of $F_2(T=\frac{1}{2}, j=0)$, which should be present according to the considerations of I (p. 489), was attributed in ref. 2 to the presence of a small $\sigma$.

*Additional representatives of types given in Table II* (brackets denote that the classification given is in the nature of a prediction based on incomplete information): Type I, AgH, AuH, and the [visible absorption bands of $Cl_2$, $Br_2$, $I_2$]; infra-red oscillation-rotation bands of HF, HCl, HBr, [CO] (except of course that there is no electronic change); Type IIa, [alkali metal absorption bands], [CO 4th positive bands], $He_2$ "main" and "second" series bands; Type IIb, $He_2$ λ6400 and λ4546; Type IV, $N_2^+$, AlO, [$CO^+$ negative Deslandres], [BOβ], and [SiN] bands; Type Va, CdH, HgH, [BOα], [red CN], [$CO^+$ comet tail]; and probably the [doublet alkaline earth halide bands]; Type *Vb*, [BO and $CO^+$ combination bands], [SnCl bands]; Type VIIa, OH bands ($^1P-{}^1S$ transition in O atom?),—but $\rho''$ and $\sigma''$ must be supposed to vary with $j''$; also CH λ4300 (perhaps $^1P-{}^3S$ transition in C atom), except that this band has 12 branches; the green MgH bands (transition 3 $^1S-3\ {}^3P_1$ in Mg atom, probably) may be classified under Type VIIb, resembling the OH and CH λ3900 bands except for a reversal of the rôles of initial and final electronic states; in all bands of Type VII, $\epsilon'\sim\epsilon''$ is here attributed essentially to the H atom in its normal state (cf. I, p. 501, under CH λ3900), while $\sigma$ is attributed primarily to the other atom.

*Additional types.* Various additional types also exist, e.g., the triplet type of the second positive nitrogen and Swan (probably $C_2$) bands (cf. above, p. 1208). These apparently require for their interpretation the assumption of a variable $\sigma$ and $\rho$, like the OH bands of Type VII.

*Some general results from Table II.* From Table II it will be seen that in $P$ and $D$ states, $j_e$ appears essentially as $\sigma$ in all cases yet known, while in $S$ states it appears in known cases as $\pm\ \epsilon$ (with $\epsilon=0$ for $^1S$ states). This rule is intimately related to recent theoretical work of Hund (cf. later paper).

A corollary of the empirical rule that $S$ states are of the $\rho$ type, combined with the specifications of the postulates in regard to $j$ and $j_e$ values, is that for such states the nuclear angular momentum $m$ (expressed in quantum units) has (approximately[43]) *half-integral* values (or integral values, if the $j$ values of the quantum mechanics are adopted, —cf. Introduction); for $P$ and $D$ states this is true only for even molecules and then only asymptotically for $j$ values so large that $m=\sqrt{j^2-\sigma^2}$ approximates $j$. These results are of obvious importance for the theory of the specific heats of diatomic gases.

In a subsequent paper it will be shown that the interpretations given above are strongly supported by observed intensity relations, which show close agreement with those to be expected from the correspondence principle.

Jefferson Physical Laboratory,
Harvard University,
July 20, 1926.

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[43] This qualification is to take account of the usual small deviations of $j_e$ from an exact integer or half-integer (cf. above[6]).