

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN  
DIATOMIC MOLECULES. V. BANDS OF THE VIOLET  
CN ( ${}^2S \rightarrow {}^2S$ ) TYPE

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ABSTRACT

Theoretical intensity formulas applicable to bands of the violet CN ( ${}^2S \rightarrow {}^2S$ ) type are obtained (cf. Eqs. 5-7 of text) with the help of the summation rules, assuming Hund's case *b* type of interaction of the electron spin. The equations predict two *Q* branches ( $Q_{1,2}$  and  $Q_{2,1}$ ), hitherto unrecognized, which should appear as weak satellite series, one accompanying the familiar double *P* branch, the other, the *R* branch. These *Q* branches should decrease in intensity from their first members. The first  $Q_{2,1}$  (or  $Q_{1,2}$ ) line should accompany the otherwise single first line of the *R* (or *P*) branch, all other *P* and *R* lines being truly double; this is in agreement with Hulthén's results on the *B* bands of CaH. For low *j* values in the *P* and *R* branches, the doublet component corresponding to the parallel orientation ( $+\epsilon$ ) of the electron spin vector should be appreciably more intense than that corresponding to the anti-parallel orientation ( $-\epsilon$ ). Treating the doublets (and their satellites) as unresolved single lines, the intensities should be exactly as in  ${}^1S \rightarrow {}^1S$  bands (CuH, HCl). The above predictions seem to be confirmed in the CaH,  $N_2^+$ , and violet CN bands. Thus the theory appears to afford a satisfactory explanation of the observed lines and intensity relations in  ${}^2S \rightarrow {}^2S$  bands, removing previous difficulties and uncertainties in interpretation.—Other  $S \rightarrow S$  transitions are treated briefly.

The nature of the energy differences between the  ${}^2S$  terms corresponding to  $+\epsilon$  and  $-\epsilon$  is considered. In all cases where the order of the terms can be determined, with the one exception of the initial states of the *B* bands of CaH, it is found that  $F_1 > F_2$ . This suggests that the magnetic field which causes  $F_1 \neq F_2$  (developed by the molecular rotation in accordance with Kemble's theory) may be in part that of the nuclei as well as of the electrons.

INTRODUCTION

EXCEPT for the fact that each line is (usually very closely) double, bands of the violet CN( ${}^2S \rightarrow {}^2S$ ) type show the same obvious structure (one *P* and one *R* branch) and intensity relations as the single-line bands of the CuH ( ${}^1S \rightarrow {}^1S$ ) type. Their doublet character was first explained by Kratzer,<sup>1</sup> who assumed the existence of an electronic angular momentum  $\epsilon = \frac{1}{2}$  which could orient itself either parallel or antiparallel ( $\rho = \pm \frac{1}{2}$ ) with respect to the axis of rotation. The probable *necessity* of Kratzer's assumption  $\rho = \pm \frac{1}{2}$  in bands of the violet CN type, and of the assumption  $\rho = 0$  in bands of the CuH type,—and of  $\sigma = 0$  in both types,—has been pointed out in a previous paper.<sup>2</sup> The interpretation of both these classes of bands in terms of Hund's theory<sup>3</sup> of molecular electronic states has been discussed by

<sup>1</sup> A. Kratzer, Münch. Ber., p. 107 (1922); Ann. der. Physik, **71**, 72 (1923).

<sup>2</sup> R. S. Mulliken, Phys. Rev. **28**, 481-506 (1926).

<sup>3</sup> F. Hund, Zeits. f. Physik **36**, 657-674 (1926).

Kemble<sup>4</sup> and by the writer.<sup>5</sup> According to the theory, the quantity  $\epsilon$  in  ${}^2S$  states represents (in quantum units) the resultant spin  $s$  of the electrons. In most cases  $s$  may be attributed to a single outer electron. The coupling of the spin corresponds to Hund's case  $b$  (or, equally well, to his case  $d$ ). Since  $\sigma_k = 0$ ,<sup>4,5</sup> we have  $m = j_k$ , where  $j_k$  is the resultant of  $m$  and  $\sigma_k$ . In other words the nuclear rotation has the same quantized values as in  ${}^1S$  states.

Although the intensity relations in  ${}^1S \rightarrow {}^1S$  bands are now well understood in terms of the new mechanics,<sup>6</sup> no satisfactory intensity formulas have yet been given for  ${}^2S \rightarrow {}^2S$  bands. Dieke<sup>7</sup> applied the summation rule to such bands on the *assumption* that they consist of double  $P$  and  $R$  branches only. In order to avoid alternating or stepwise-advancing intensities (in the individual branches) he was forced to assume a priori probabilities  $p = 2j - 1$ . This is open to serious theoretical objections, especially since in atomic spectra the relation  $p = 2J$  holds for both odd and even multiplicities, and since the corresponding relation  $p = 2j$  has been confirmed for both singlet and doublet electronic states of the  $\sigma$  type in molecules ( $J = \text{Landé's } J$ )<sup>8,9</sup>.

Dieke's theory makes the first line in each branch single, by excluding, as did Kratzer, the state  $j = 0$ ; but recent experimental work of Hulthén on the  $B$  bands of CaH shows<sup>10</sup> that this line is double like the remaining lines.—According to Dieke's theory, the relative intensities of successive (unresolved double) lines in each branch should be in the ratio 1:3:5: . . . , as compared with 2:4:6: . . . in  ${}^1S \rightarrow {}^1S$  transitions.

It now appears that the difficulties mentioned above can be avoided only by giving up the assumption that bands of the violet CN type contain  $P$  and  $R$  branches only. In fact Dieke himself suggested<sup>7</sup> that in the CN doublets, one doublet component might represent a true  $P$  or  $R$  line, the other (by assuming  $\Delta\rho = \pm 1$ ) a  $Q$  line. As will be shown below, a satisfactory explanation of the structure and intensity relations follows very simply if the bands are treated as an example of Hund's case  $b$ .

#### THEORY OF STRUCTURE AND INTENSITY RELATIONS

*General.* The theoretical intensity formulas for any transition between two electronic states both of which fall under Hund's case  $b$  can be obtained in two steps, as follows: (1) For a given value of  $\Delta\sigma_k$ , the relative intensities corresponding to the three cases  $\Delta j_k = 0, \pm 1$  can be expressed as functions of  $j_k$  and  $\sigma_k$ , if the fine structure due to the interaction of  $j_k$  and  $s$  be neglected. These functions should be identical in form with those (the Hönl and London equations<sup>6</sup>) which are applicable for  $\Delta j = 0, \pm 1$  in Hund's case  $a$ . It is then

<sup>4</sup> E. C. Kemble, Nat. Res. Council Bulletin on Molecular Spectra, pp. 326–331 and 345–47 (No. 57, Dec., 1926).

<sup>5</sup> R. S. Mulliken, Phys. Rev. **29**, 637 (1927).

<sup>6</sup> Cf. refs. and discussion in ref. 8.

<sup>7</sup> G. H. Dieke, Nature **115**, 875 (1925); Zeits. f. Physik **33**, 161 (1925).

<sup>8</sup> R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

<sup>9</sup> F. A. Jenkins, H. A. Barton and R. S. Mulliken, Nature **119**, 118 (1927); Phys. Rev. **30**, 150 (1927).

<sup>10</sup> E. Hulthén, Phys. Rev. **29**, 97 (1927).

necessary only to substitute  $j_k$  and  $\sigma_k$  for  $j$  and  $\sigma$  in the appropriate Hönl and London equations. (It may be noted that, unlike case  $a$ ,  $\sigma$  cannot differ<sup>5</sup> from  $\sigma_k$  in case  $b$ ). The truth of these statements follows from the fact that the correspondence principle expressions are of the same form and type in the two cases,<sup>5</sup> so that the "sharpening" of these to the corresponding summation rule expressions must evidently proceed in the same manner in both. Further, the summation rule expressions of Hönl and London remain valid in the new mechanics.<sup>11</sup>

(2) The intensities obtained in (1) must now be subdivided corresponding to the fine structure arising from the interaction of  $j_k$  and  $s$ . This interaction is precisely analogous<sup>3,4,5</sup> to that of  $k$  and  $s$  in atomic spectra, and, as in the latter, the various possible orientations of  $s$  with respect to  $j_k$  should yield a set of levels with different  $j$  values, constituting a multiple term. The relative intensities of transitions involving different values of  $\Delta j$  and of  $j'$  (or  $j''$ ) should then be given, for any fixed values of  $\Delta j_k$  and of  $j_k'$  (or  $j_k''$ ), by exactly the same expressions as for line spectrum multiplets, if merely  $j_k$  be substituted for  $k$  in the formulas for the latter. The equations obtained by Kronig and by Sommerfeld and Hönl<sup>12</sup> are applicable here; as has been shown by Dirac,<sup>13</sup> the same expressions can be obtained from the new mechanics.

By combining the results of (1) and (2), complete explicit expressions for the intensities of all band lines should be obtainable for case  $b$ , although in practise these may sometimes prove too cumbersome. For case  $a$ , the theoretical intensity relations are given by the Hönl and London equations.<sup>6,5</sup> (In both cases, vibration and other disturbing factors are here neglected). The proper procedure for obtaining accurate equations in cases intermediate between  $a$  and  $b$  is not yet evident.

*Application to  ${}^2S \rightarrow {}^2S$  transitions.*—In the present paper, only  $S \rightarrow S$  transitions, in particular  ${}^2S \rightarrow {}^2S$ , will be considered. In all these a close approximation to the ideal case  $b$  may be expected, except that in some cases the energy of interaction of  $j_k$  and  $s$  may be so small (especially for low  $j_k$  values) that the orientation of  $s$  with respect to  $j_k$  is not quantized.

In  $S \rightarrow S$  transitions in general,  $\Delta\sigma_k = \sigma_k' = \sigma_k'' = 0$ , and, in terms of  $j_k$  and  $\Delta j_k$ , the intensities should be exactly as in  ${}^1S \rightarrow {}^1S$  transitions. Since in  $S$  states,  $j_k = m = T$ , and since the arrangement of the band lines on a frequency scale is determined<sup>2</sup> by  $T$  and  $\Delta T$ , this means that all  $S \rightarrow S$  transitions should be identical in obvious structure and intensity relations, if the fine structure is neglected. In all such transitions, there should be only a  $P$ -form and an  $R$ -form branch ( $\Delta j_k = \pm 1$ ); these should be at least approximately continuous except for a central missing line. The intensities of suc-

<sup>11</sup> D. M. Dennison, Phys. Rev. **28**, 329 (1926); R. de L. Kronig and I. I. Rabi, Phys. Rev. **29**, 262 (1927); F. Reiche, Zeits. f. Physik **39**, 444 (1926); H. Rademacher and F. Reiche, Zeits. f. Physik, **41**, 453 (1927). Cf. ref. 25 of ref. 5.

<sup>12</sup> R. de L. Kronig, Zeits. f. Physik **31**, 885 (1925); A. Sommerfeld and H. Hönl, Sitzungsber. der Preuss. Akad. der Wiss., phys.-math. Klasse, p. 141 (1925).

<sup>13</sup> P. A. M. Dirac, Proc. Roy. Soc. London, *A* . . . . . (192-).

cessive lines in each branch, aside from the Boltzmann factor, should be<sup>6,14</sup> in the ratio 2:4:6: . . . (cf. Fig. 1a), as given by the equation<sup>15</sup>

$$i = 2j_k \quad (1)$$

We have now to find how the line corresponding to any pair of values ( $j_k', j_k''$ ) is split into components. There are two cases to be considered, namely those for which  $\Delta j_k = +1$ , and those for which  $\Delta j_k = -1$ . These correspond to  $\Delta k = +1$  and  $\Delta k = -1$  in line spectra. Sommerfeld and Hönl give equations (Eqs. 5-6 of their paper<sup>12</sup>) which cover both cases at once.

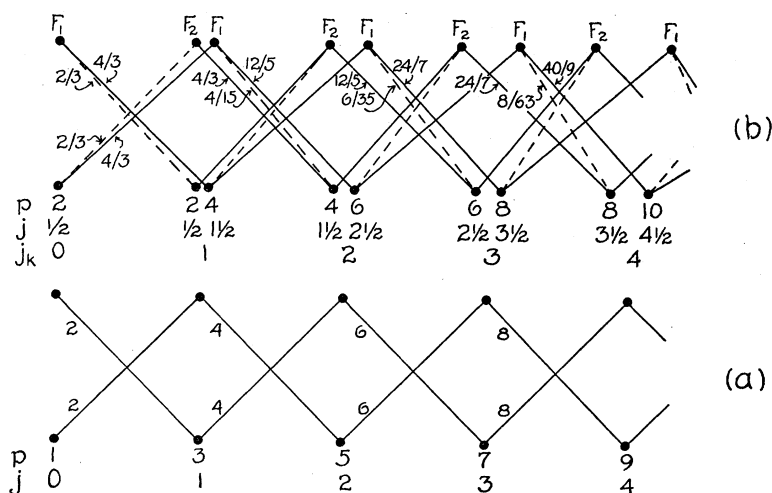


Fig. 1b shows diagrammatically the possible transitions and their relative intensities (neglecting the Boltzmann factor) near the origin of a typical  $^2S \rightarrow ^2S$  band. The a priori probabilities  $p$  and the  $j$  and  $j_k$  values refer both to the initial (upper row of dots) and final (lower row) states. In regard to the actual magnitude of separation, and order, of the levels  $F_1$  and  $F_2$ , cf. Fig. 2 description, and text. The intensities, calculated from Eqs. 5-7, are indicated by figures adjacent to the appropriate lines. The intensities which are not given are the same as those for lines which differ only in respect to interchange of initial and final values of  $j$  and  $j_k$  (e.g., the transition  $R_2(1\frac{1}{2})$ , with  $j' = 2\frac{1}{2}$ ,  $j'' = 1\frac{1}{2}$ ,  $j_k' = 3$ ,  $j_k'' = 2$  has the same intensity as  $P_2(2\frac{1}{2})$  with  $j' = 1\frac{1}{2}$ ,  $j'' = 2\frac{1}{2}$ ,  $j_k' = 2$ ,  $j_k'' = 3$ ). The Q branches are shown by dashed lines.

Fig. 1a is typical for a  $^1S \rightarrow ^1S$  band. Fig. 1b can be derived from it by suitable sub-division of the levels and of the transitions and their intensities. E.g., the sum of the intensities for the three transitions corresponding to  $j_k' = 2$ ,  $j_k'' = 3$  is the same, namely 6, in Fig. 1b as the intensity of the single transition in Fig. 1a.

After replacing  $k(j_a$  of Sommerfeld and Hönl) by  $j_k$  and also replacing Sommerfeld's  $j_s$  and  $r = 2j_s + 1$  by their equivalents in the present notation, namely  $s$  and  $2s + 1$ , and after dropping a factor  $(2s + 1)/4$  which is common

<sup>14</sup> Cf. also R. T. Birge, Bull. Mol. Spectra, pp. 218-19.

<sup>15</sup> This corresponds, with the conventions and  $j$  numbering adopted here, to Eq. (2) of ref. 8, except for the omission of a proportionality factor  $a$ ;  $j_k$  in Eq. (1) represents the larger of the quantities  $j', j''$ .

to all the equations and therefore is of no significance for the present purpose, these equations are as follows:

For  $j \rightarrow j-1$ , if  $j_k \rightarrow j_k-1$ ; or equally, for  $j-1 \rightarrow j$ , if  $j_k-1 \rightarrow j_k$ ,

$$i^\pm = [(j+j_k)(j+j_k+1) - s(s+1)][(j+j_k-1)(j+j_k) - s(s+1)]/jj_k \quad (2)$$

For  $j \rightarrow j$ , for either  $j_k \rightarrow j_k-1$  or  $j_k-1 \rightarrow j_k$ ,

$$i^0 = (2j+1)[(j+j_k)(j+j_k+1) - s(s+1)][s(s+1) - (j-j_k)(j-j_k+1)]/jj_k(j+1) \quad (3)$$

For  $j-1 \rightarrow j$ , if  $j_k \rightarrow j_k-1$ , or for  $j \rightarrow j-1$  if  $j_k-1 \rightarrow j_k$ ,

$$i^\mp = [s(s+1) - (j-j_k)(j-j_k+1)][s(s+1) - (j-j_k-1)(j-j_k)]/jj_k \quad (4)$$

In these equations,  $j_k$  evidently always represents the larger of the two quantities  $j_k'$  and  $j_k''$ ; similarly with  $j$ . The  $j$  and  $j_k$  values correspond to

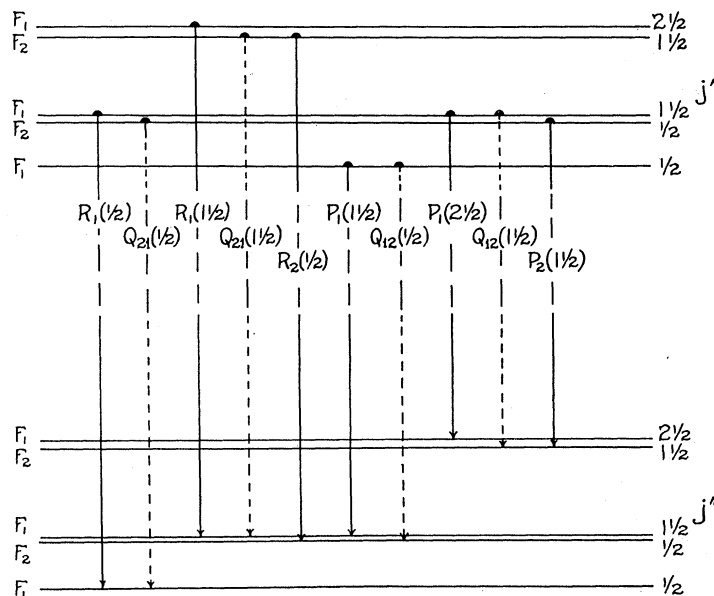


Fig. 2 illustrates the arrangement of the energy levels, and the relative positions on a frequency scale of the band lines, for a  ${}^2S \rightarrow {}^2S$  transition. Only a few of the lowest levels are shown here. The relative positions of  $P_1$  and  $P_2$ ,  $R_1$  and  $R_2$  lines, and their "satellites" ( $Q$  lines) can be seen by a study of the diagram. In practise the doublet separation  $F_1 - F_2$  is usually greater for the initial than for the final state, but sometimes the reverse is true (cf. text). Except for the hydrides, the separation  $F_1 - F_2$  is ordinarily too small to be detected for low values of  $j$ . Sometimes (initial state of  $B$  bands of CaH) the order  $F_2 > F_1$  replaces the usual  $F_1 > F_2$ . The effect of the various possibilities mentioned on the experimental appearance of the band structure can be seen by a study of the figure.

Sommerfeld's  $j$  numbering, and therefore to that of the new mechanics, and so are all  $\frac{1}{2}$  unit lower than those used in previous papers of this series. *The new  $j$  numbering* has real advantages for the present discussion and so *will be adopted here.*

Now let us consider the typical transition  $j_k - 1 \rightarrow j_k$  (e.g.  $1 \rightarrow 2$ ), or  $j_k \rightarrow j_k - 1$  (e.g.  $2 \rightarrow 1$ ). Since  $s = \frac{1}{2}$  here,  $j$  has two values  $j_k \pm \frac{1}{2}$  for each value of  $j_k$  (cf. Fig. 1b). Three transitions are possible, according to the selection rule  $\Delta j = 0, \pm 1$ , for either of the  $j_k$  transitions mentioned. Thus for the  $j_k$  transition  $1 \rightarrow 2$ , the  $j$  transitions would be  $1\frac{1}{2} \rightarrow 2\frac{1}{2}$  (a  $P_1$  line),  $\frac{1}{2} \rightarrow 1\frac{1}{2}$  (a  $P_2$  line), and  $1\frac{1}{2} \rightarrow 1\frac{1}{2}$  (a  $Q_{1,2}$  line); while for the  $j_k$  transition  $2 \rightarrow 1$ , the  $j$  transitions would be  $2\frac{1}{2} \rightarrow 1\frac{1}{2}$  (an  $R_1$  line),  $1\frac{1}{2} \rightarrow \frac{1}{2}$  (an  $R_2$  line), and  $1\frac{1}{2} \rightarrow 1\frac{1}{2}$  (a  $Q_{2,1}$  line); cf. Fig. 2. The subscript notation used here involves an extension to the  $Q$  branches of that already adopted,<sup>2</sup> following Kratzer, to distinguish between the  $j_k + \epsilon$  (sub-1) and the  $j_k - \epsilon$  (sub-2) terms; the first and second subscripts of  $Q$  refer to the initial and final states respectively in emission.

The relative intensities of the three components associated with each  $j_k$  transition are determined by Eqs. (2) and (3),—no transition corresponding to Eq. (4) is possible in the present case,—while the sum of their intensities must be, in accordance with Eq. (1), proportional to  $j_k$ . These conditions can evidently be met in the following way. Analytical expressions giving the relative intensities of the three fine-structure components are written down in accordance with Eqs. (2) and (3), making in each equation the substitution  $s = \frac{1}{2}$ , and also substituting  $j_k + \frac{1}{2}$  or  $j_k - \frac{1}{2}$  for  $j$ . After simplifying, and omitting a common factor 8, the three resulting equations are as follows:

$$P_1 \text{ or } R_1(j = j_k + \frac{1}{2}) \quad i_1 = (j_k + 1)(2j_k - 1) \quad (2a)$$

$$P_2 \text{ or } R_2(j = j_k - \frac{1}{2}) \quad i_2 = (j_k - 1)(2j_k + 1) \quad (2b)$$

$$Q_{1,2} \text{ or } Q_{2,1}(j = j_k - \frac{1}{2}) \quad i_3 = 1 \quad (3a)$$

The sum of the expressions  $i_3$ ,  $i_1$ , and  $i_2$  is  $(4j_k^2 - 1)$ . Then if each of the equations (2a), (2b), (3a) is multiplied by  $2j_k/(4j_k^2 - 1)$ , the final expressions for the relative intensities of the individual components are obtained. By substitution for  $j_k$  in terms of  $j$  these are reduced to a very simple form. Both forms are given in the following equations.—It should be remembered that the  $j$  and  $j_k$  values in these equations refer to the larger of the two quantities  $j_k'$  and  $j_k''$ , or  $j'$  and  $j''$ . In calculating actual band intensities, the Boltzmann factor must of course be introduced.<sup>6</sup>

$$P_1 \text{ or } R_1: i_1 = 2j_k(j_k + 1)/(2j_k + 1) = (j^2 - \frac{1}{4})/j \quad (5)$$

$$P_2 \text{ or } R_2: i_2 = 2j_k(j_k - 1)/(2j_k - 1) = (j^2 - \frac{1}{4})/j \quad (6)$$

$$Q_{1,2} \text{ or } Q_{2,1}: i_3 = 2j_k/(4j_k^2 - 1) = (2j + 1)/4j(j + 1) \quad (7)$$

That these equations satisfy the summation rule (sum of intensities of transitions to or from a given state equal to a priori probability  $p(=2j+1)$  of that state) can readily be verified from the equations or from Fig. 1b. In this figure the various possible transitions and their relative intensities in accordance with Eqs. (5–7) are shown diagrammatically, for a typical  ${}^2S \rightarrow {}^2S$  transition.

The most striking result of the preceding analysis is the prediction of the existence of two weak  $Q$  branches in addition to the strong double  $P$  and  $R$  branches hitherto generally supposed to be alone present. As a result, the difficulties inherent in Dieke's theory are avoided. Another result is that for low values of  $j_k$  there should be an appreciable inequality in the intensities of the components of any  $P$  or  $R$  doublet, the  $P_1$  or  $R_1$  component being the stronger, approximately in the ratio of the  $j$  values. For large  $j_k$  values, the two components should be asymptotically equal in intensity.

*Other  $S \rightarrow S$  transitions.*—By similar methods, the possible branches and their relative intensities can be predicted in detail for other  $S \rightarrow S$  transitions, such as  ${}^3S \rightarrow {}^3S$ ,  ${}^3S \rightarrow {}^1S$ ,  ${}^4S \rightarrow {}^4S$ , etc. The intense branches should be those for which  $\Delta j = \Delta j_k = \pm 1$ , additional branches appearing as weak satellite series. The subscript notation adopted above can be readily extended, using e.g.  $F_1$ ,  $F_2$ , and  $F_3$  for the three possible orientations of  $s$  in a  ${}^3S$  state. In general, double subscripts will be needed for  $P$  and  $R$  as well as  $Q$  branches.

#### COMPARISON OF THEORY WITH EXPERIMENT

*General.* Except for the first line in each, the predicted intensities of the  $Q$  branches are so low that these branches would as a consequence almost certainly pass unnoticed, and in fact usually be undetectable. Furthermore, in the usual case that the ( $P$  and  $R$ ) doublets are unresolved for low  $j_k$  values, the  $Q_{1,2}$  and  $Q_{2,1}$  branches would not be resolved from the  $P$  and  $R$  branches respectively (cf. Figs. 1b and 2). Even if the doublets are resolved, the  $Q$  branches will still fall together with one or the other component (cf. Figs. 1b and 2) of the  $P$  or  $R$  branches unless appreciable term separations of doublets are present in *both initial and final* electronic states. It is therefore not surprising that these  $Q$  branches have not been observed in practise.

The first line of each  $Q$  branch is of special interest. In terms of the  $j_k$  ( $=m$ ) numbering used by Kratzer<sup>1</sup> and in previous papers of this series, the lowest rotational state was supposed to have  $j_k = \frac{1}{2}$ , so that one expected from it two rotational sub-states  $F_1(1)$  and  $F_2(0)$ . Kratzer assumed that  $F_2(0)$  should be ruled out, so that the first line of each branch should consist of a  $P_1$  or  $R_1$  component only. This question has subsequently been discussed by Birge<sup>16</sup> and Dieke.<sup>7,17</sup> The writer argued<sup>2</sup> against the exclusion of  $F_2(0)$  as arbitrary, and concluded that the first line in each branch should have two components. With the change of numbering introduced by the new mechanics, the question appears in a new light. With  $j_k = 0$  for the lowest rotational state, only the one rotational sub-state  $F_1(\frac{1}{2})$  is possible, and the first  $P$  or  $R$  line should be single ( $P_1$  or  $R_1$  only),—in agreement with Kratzer. But these lines should *appear* double like the other  $P$  and  $R$  lines (cf. Figs. 1b and 2) on account of the here relatively intense  $Q_{1,2}$  and  $Q_{2,1}$  lines which accompany them. Thus a perplexing difficulty is removed, in a way which emphasizes the superiority of the  $j$  numbering of the new mechanics.

<sup>16</sup> R. T. Birge, Bull. Mol. Spectra, pp. 185, 203, 218.

<sup>17</sup> G. H. Dieke, Physica 5, 178 (1925).

CaH bands. The best available test of the theory is afforded by the  $B$  bands of CaH, two of which ( $B$  and  $B'$ ) were measured and analyzed by Hulthén.<sup>10</sup> In these bands the  $P$  and  $R$  doublets are much wider than for any other  ${}^2S \rightarrow {}^2S$  transition on record, and are resolved down to the first line. In the stronger ( $B$ ) band, the first line of the  $R$  branch appears double like the rest, as predicted; likewise in the first  $P$  line a relatively high intensity indicates, according to Hulthén, the presence of two unresolved components. In the weaker ( $B'$ ) band, the first three  $R_2$  and the first four  $P_2$  lines are unrecorded in Hulthén's table, indicating that they are comparatively weak, as predicted by the theory; the expected  $P_1$  and  $R_1$  lines are recorded (unfortunately Hulthén gives no explicit intensity data). That Hulthén's  $P_1$  and  $R_1$  lines really correspond to  $+\epsilon$  and his  $P_2$  and  $R_2$  lines to  $-\epsilon$  is shown through combination relations with the  $A$  bands of CaH (cf. a following paper of this series); without these combinations it would be impossible to make this identification from the structure alone, although the identification could be made by assuming the correctness of the intensity theory.

Hulthén's " $R_2(0)$ ," the high frequency component of the first  $R$  line in the  $B$  band, should evidently be classified according to the theory as  $Q_{2,1}(\frac{1}{2})$ , the low frequency component " $R_1(1)$ " being  $R_1(\frac{1}{2})$  in the new  $j$  numbering. As can be seen from Figs. 1b and 2, the doublet separation  $R_1(\frac{1}{2}) - Q_{2,1}(\frac{1}{2})$  should measure directly the term separation,  $F_1'(1) - F_2'(1)$  for  $j_k' = 1$ ; experimentally this amounts to  $-1.26$  wave-number units. Hulthén's " $P_2(1)$  plus  $P_1(2)$ " (unresolved) should be classified as  $Q_{1,2}(\frac{1}{2})$  plus  $P_1(1\frac{1}{2})$ ; their separation, here too small to measure, should represent directly the term separation  $F_1''(1) - F_2''(1)$ . No lines are recorded by Hulthén which can be identified as additional members of the  $Q$  branches. Further experimental work with longer exposures and higher dispersion should disclose some of these lines; a careful study of the intensity relations would also be very desirable.

Making use of the four sets of  $\Delta_2 F$  values (for definition of  $\Delta_2 F$  cf. ref. 2, p. 490) established by Hulthén from combination relations, and of the separations  $F_1' - F_2'$  and  $F_1'' - F_2''$  for  $j_k = 1$  as obtained above, the term-separations  $F_1 - F_2$  can be calculated for any odd value of  $j_k$ . Hulthén gives  $\Delta_2 F_1''(j+1) - \Delta_2 F_2''(j) \sim 0.09$ , from which it follows that  $F_1'' - F_2'' \sim +0.0225 j_k''$ . But  $\Delta_2 F_1'(j+1) - \Delta_2 F_2'(j)$  has much larger values, of *opposite sign*, e.g.  $-2.34$  for  $j = 1\frac{1}{2}$  (i.e.,  $[F_1'(3\frac{1}{2}) - F_1'(1\frac{1}{2})] - [F_2'(2\frac{1}{2}) - F_2'(1\frac{1}{2})] = -2.34$ ); the numerical value of this difference decreases, at first rapidly, then more and more slowly, with increasing  $j$ , the difference approaching a value of about  $-1.0$  for  $j \sim 30$ . Hence, starting from  $F_1'(1) - F_2'(1) = -1.26$  for  $j_k' = 1$ , we get  $F_1'(3) - F_2'(3) = -3.60$ , and so on, the differences increasing steadily with  $j$ .

The  $C$  band of CaH, measured and analyzed by the writer,<sup>18</sup> has been shown by Hulthén to have the same set of final rotational states as the  $F_2''$  states of the  $B$  bands. The initial states of the  $C$  bands are then presumably

<sup>18</sup> R. S. Mulliken, Phys. Rev. 25, 509 (1925).



$F_2'$  states of a  ${}^2S$  type. The complete absence of  $F_1'$  states is puzzling, but is perhaps connected with the extreme instability of the molecule<sup>18</sup> in the initial electronic state of the  $C$  band.

*AIO bands.* In the AIO bands, as investigated by Pomeroy,<sup>19</sup> the doublets are resolved only for high values of  $j$ , so that no evidence is available as to the presence of  $Q$  branches or as to the relative intensities of the  $P$  and  $R$  doublet components for low  $j$  values. The intensities of the doublet components are equal for high  $j$  values (private communication from Professor R. T. Birge) in agreement with the theory.

The doublet separation is mainly or wholly confined to the *final* electronic state, as is shown by equality of corresponding doublet separations in the  $(0, 0)$  and  $(1, 0)$  bands.<sup>19</sup> The separation increases nearly linearly with  $j_k$  (slightly faster for  $j_k > 100$ ), from about 0.40 wave-number units at  $j_k = 28$  to 1.90 units at  $j_k \sim 135$ . Whether  $F_1''$  or  $F_2''$  is greater cannot be decided from the data, since there is no way of determining how the subscripts 1 and 2 should be assigned to the observed doublet components.

*Violet CN bands.* The violet CN bands are the classical example of a  ${}^2S \rightarrow {}^2S$  transition.<sup>1,2,20</sup> The doublets are not resolved for the smallest values of  $j$ , but examination of plates taken by the writer shows indications of slight inequality of the doublet components near where they are first resolved, also some indication of weak satellites; however, this is uncertain.

The doublet width shows conspicuous perturbations which are characteristic for given values of  $n'$  and  $j'$ ,<sup>21</sup> so that a considerable doublet separation certainly exists in the initial states.<sup>20</sup> There is at present no means of deciding whether or not a (probably smaller) separation also exists in the final states. The observed doublet separation in each branch increases more or less linearly with  $j_k$  at first, reaches a maximum at about  $j_k = 75$ , and then decreases;<sup>22</sup> if, as in AIO, the term-separation increases somewhat faster than linearly for large  $j_k$  values, and if this effect is more pronounced in the final state, so that the final term-separations, although comparatively small at first, approach the initial term-separations for high  $j_k$  values, the observed relations would be accounted for. There is no means of deciding, from existing data, the proper assignment of the subscripts 1 and 2, or the order of  $F_1$  and  $F_2$  levels. An analysis of the red CN bands, now in progress in this laboratory, may help to remove the above uncertainties.

As already noted above (p. 140), the intensity relations should be exactly the same in  ${}^2S \rightarrow {}^2S$  as in  ${}^1S \rightarrow {}^1S$  transitions (cf. ref. 8, p. 398-9, 401-2 in regard to the latter) if the fine structure is neglected. From this point of view, the violet CN bands show fairly good agreement with the theory: the intensity at first increases symmetrically in the two branches, approximately linearly with  $j_k$ , but is brought to a maximum by the Boltzmann factor, this maximum depending on the temperature, and being higher

<sup>19</sup> W. C. Pomeroy, Phys. Rev. **29**, 59 (1927).

<sup>20</sup> R. T. Birge, Bull. Mol. Spectra, pp. 182-87, 215-21, etc.

<sup>21</sup> T. Heurlinger, Dissertation Lund, 1918.

<sup>22</sup> R. T. Birge, Astrophys. J. **55**, 273 (1922).

(cf. ref. 8 in regard to theory) in the  $P$  than in the  $R$  branch.<sup>20</sup> This is shown especially by the work of Birge.<sup>22</sup>

Sewig<sup>23</sup> also has made a photometric study of the intensity relations in these bands in various sources. According to him, the intensities of the  $P$  and  $R$  branches rise at first symmetrically from the missing line, as predicted, but the intensities for the first few lines are more nearly in the ratio 6:8:10 than in the theoretical ratio 2:4:6 (the agreement is evidently better with the present theory, however, than for Dieke's predicted ratios<sup>8</sup> 1:3:5,—cf. introduction). It seems possible that Sewig's measurements have been overcorrected in the case of weak lines; further experimental work would be very desirable. Sewig finds the  $R$  branch stronger than the  $P$  branch in  $\lambda 4216$ , and the two branches about equally intense in  $\lambda 3883$ .

$N_2^+$  bands.—In the case of the  $N_2^+$  bands, Fassbender's work<sup>24</sup> shows that a term doublet separation exists in the initial states: there are perturbations in the line doublet separations which are the same for all bands having the same  $n'$ . The doublet separations are irregular on account of these perturbations, and larger for  $n'=1$  than for  $n'=0$ .

On plates taken by the writer in the second order of the 21 foot concave grating at Harvard University, the high-frequency components of the doublets are decidedly more intense than the low-frequency components for low values of  $j_k$  (the doublets begin to be resolved at about  $j_k=10$ ), while this difference becomes imperceptible as  $j_k$  increases (the bands examined were  $\lambda 3914$  and  $4278$ ). In a weak third order exposure of  $\lambda 3914$ , the differences for the lower values of  $j_k$  are rather marked, probably because of increased photographic contrast. If this evidence is valid (it cannot be regarded as quite certain because of the possibility of slight out-of-focus phenomena, and should be checked by other observers), it shows, assuming the correctness of the intensity theory and granting that the doublet separations are mainly due to the initial states, that  $F_1' > F_2'$ .

Photometric measurements on the  $N_2^+$  band  $\lambda 3914$  (doublets not resolved) have been made by Sewig.<sup>23</sup> The agreement with theory is similar to that in the violet CN bands. The  $P$  branch is, however, definitely more intense than the  $R$  branch here, according to Sewig,—in agreement with earlier results of Fassbender. The alternating intensity of successive doublets in the  $N_2^+$  bands (which does not particularly concern us here) is fairly well taken care of by introducing into the intensity equations a factor of about 1.5 for alternate lines.

ZnH, CdH, HgH, MgH, OH bands. While  ${}^2S \rightarrow {}^2S$  transitions are not yet on record for the molecules named, their  ${}^2P \rightarrow {}^2S$  or  ${}^2S \rightarrow {}^2P$  bands give valuable information in regard to the doublet separations in  ${}^2S$  states. In  ${}^2P \rightarrow {}^2S$  transitions, the assignment of the subscripts 1 and 2 for the  ${}^2S$  states can be made definitely on the basis of the combination relations together with the safe assumption that  $\Delta j$  is confined to the values 0,  $\pm 1$ . In ZnH,

<sup>23</sup> R. Sewig, Zeits. f. Physik **35**, 511 (1926).

<sup>24</sup> M. Fassbender, Zeits. f. Physik **30**, 73 (1924).

CdH, and HgH, as shown by the work of Hulthén<sup>25</sup> and Kratzer,<sup>1</sup>  $F_1(j_k) > F_2(j_k)$ ; approximately,  $F_1(j_k) = Bm^2 + km$ ,  $F_2(j_k) = Bm^2 - km$ .<sup>26</sup> The coefficient  $k$  is large for HgH, less for CdH, still less for ZnH.<sup>1</sup> In HgH, the initial rate of increase of  $F_1 - F_2$  with  $j_k$  is not maintained; for  $m = 26$ , the rate of increase has fallen nearly to zero (cf. Table 9 of ref. 1). The data of Watson and Rudnick<sup>27</sup> on MgH also strongly indicate  $F_1 > F_2$ , the difference  $F_1 - F_2$  being rather small. The relation  $F_1 > F_2$  again holds in the initial  $^2S$  state of the OH bands (cf. following paper); in the initial state of CH  $\lambda 3900$  the order of the levels is doubtful.

#### NATURE OF ENERGY DIFFERENCES BETWEEN $F_1$ AND $F_2$ TERMS IN $^2S$ STATES

Since, as Hund points out,<sup>3</sup> the electron spin probably interacts only magnetically, the energy differences between  $F_1$  and  $F_2$  terms in  $^2S$  states should be attributed to interaction of  $s$  with a magnetic field. As Kemble has shown (ref. 3, pp. 345-7), a small electronic orbital angular momentum  $\epsilon_k$  and a corresponding magnetic field, both of which should be parallel and proportional to  $m$ , are to be expected for a rotating molecule, even if the electronic angular momentum and magnetic field are zero for the non-rotating molecule. The effect is analogous to that of the Larmor precession in the theory of diamagnetism. According to this theory,  $j_k = m + \epsilon_k$ : a small fraction of the molecular angular momentum, proportional to their share of the total moment of inertia, is assigned to the electrons. The theory accounts<sup>3</sup> for the observed initially approximately linear increase with  $j_k$  in the energy differences  $F_1 - F_2$ , and also for the slightly unsymmetrical deviations, for  $F_1$  and  $F_2$  terms, of  $T$  from exact half-integral values, as found by Birge<sup>28</sup>.

In every case where definite conclusions can be drawn (according to the results summarized in the preceding paragraphs), except that of the initial states of the  $B$  bands of CaH,  $F_1 > F_2$ , i.e., the antiparallel ( $F_2$ ) orientation of  $s$  and  $m$  is the more stable. This relation is the reverse of the ordinary relation for a magnet in an external field, but corresponds to that in ordinary atomic multiplets and in most molecular  $^2P$  states. The observed relation in such multiplets is, however, theoretically the correct relation if the interaction is essentially that of the spinning electron in the field due to its own orbital motion.<sup>29</sup> In the present case, the opposite, or normal, magnetic interaction would at first sight seem more probable, since only a small part of  $\epsilon_k$  would ordinarily belong to the electron to which  $s$  belongs. However, the association of the electron spin with the field of its own orbital motion (if any) is so much closer than with the field due to other

<sup>25</sup> E. Hulthén, *Zeits. f. Physik* **11**, 284 (1922); Dissertation Lund, 1923; *Zeits. f. Physik* **32**, 32 (1925); etc.

<sup>26</sup> For further details, cf. also R. T. Birge, *Bull. Mol. Spectra*, pp. 177-86.

<sup>27</sup> W. W. Watson and P. Rudnick, *Astrophys. J.* **63**, 20 (1926); *Phys. Rev.* **29**, 413 (1927).

<sup>28</sup> R. T. Birge, *Bull. Mol. Spectra*, p. 175, 164, etc.

<sup>29</sup> W. Heisenberg and P. Jordan, *Zeits. f. Physik* **37**, 263 (1926); cf. F. Hund, *Linienpektren*, J. Springer, Berlin (1927).

electrons that the corresponding magnetic energy might well preponderate over the energy of interaction with all other electrons.

An additional possibility of explanation appears in the magnetic field of the rotating nuclei. Since nuclei and electrons have the same angular velocity<sup>30</sup> and approximately the same charges and mean distances from the center of gravity, they should produce oppositely directed fields of the same order of magnitude. It seems quite possible that the nuclear field might predominate, at least in certain regions of the molecule, and thus account for the order  $F_1 > F_2$ .<sup>31</sup>

The very marked  $F_2' > F_1'$  in the *B* bands of CaH suggests that the  $^2S$  state here is of an unusual type. Perhaps it constitutes an example of the case<sup>3</sup>  $\sigma_k \neq k$ ; perhaps this molecular  $^2S$  state is derived from one of the low-lying *P* and *D* states of the Ca atom.

The writer wishes to express his appreciation of helpful suggestions made by Professor J. H. Van Vleck.

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April 9, 1927.

<sup>30</sup> This is, of course, superposed on the orbital angular velocity of the electrons, but, as in the case of the Larmor precession in the theory of diamagnetism, this initial motion does not affect the result.

<sup>31</sup> (Added in proof). Cf. F. Hund, *Zeits. f. Physik* **42**, 96 (1927), who considers only the nuclear field.