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# ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. IV. HUND'S THEORY; SECOND POSITIVE NITROGEN AND SWAN BANDS; ALTERNATING INTENSITIES

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## Abstract

After a brief review of Hund's theory of molecular electronic states and band spectra, and a discussion of intensity relations and selection principles in terms of the correspondence principle, it is shown that practically all the available evidence, as embodied in previous papers of this series and elsewhere, is in agreement with the theory. The occurrence of $\rho$-type $S$ terms and $\sigma$-type $P$ and $D$ terms is explained by the theory, as also the existence of $\rho$-type and $\sigma$-type doubling. Selection rules and other relations in ${}^2P \rightarrow {}^2S$ and ${}^2S \rightarrow {}^2P$ transitions (including, in agreement with Mecke and Hulthén, the CH, OH, MgH, and CaH bands) are discussed. Hund's interpretation of the second positive nitrogen bands as a ${}^3P \rightarrow {}^3P$ transition is further developed, and extended to the Swan bands; the apparent absence of $Q$ branches, and other intensity relations in these bands, are explained; the rotational doubling in these bands (accompanied by alternating intensities) is interpreted as $\sigma$-type doubling. It is shown that the alternating intensities or alternate missing lines in the $He_2$, $N_2$, Swan, and $N_2^+$ bands can all be accounted for formally by the postulate that they are due to alternate (partially or completely) suppressed levels such that the suppressed values of $(j_k - \sigma_k)$ are always as follows: $B$ rotational sub-states, $(j - \frac{1}{2} - \sigma_k) = 0, 2, 4, \cdots$; $A$ sub-states, $1, 3, 5, \cdots$; here $\sigma_k$ is the part of $\sigma$ which is due to the orbital angular momentum of the electron, and $j_k$ is the resultant of $\sigma_k$ and the quantity $m$ which measures the nuclear angular momentum in quantum units.—Finally, the questions of term-notation and -formulation, $j$ values for odd and even molecules, etc., are considered. The NH $\beta$ bands (${}^3P \rightarrow {}^3S$) are briefly discussed.

*Introduction—Review of Hund's Theory.* In a very important paper,[1] Hund has discussed from a theoretical standpoint the question of the nature of molecular electronic states, by a consideration of the orders of magnitude of the various electrical and magnetic interactions to be expected in a system composed of electrons and two nuclei.

Hund assumes that, as in atomic spectra, each electron (in particular, the $\tau$'th electron) has orbital angular momentum corresponding to the (azimuthal) quantum number $k$, and in addition, a half-quantum $(s = \frac{1}{2})$ of spin angular momentum; the resultant of all the $k_\tau$'s is denoted $k$, and that of the $s_\tau$'s is denoted $s$.

Hund shows that in ordinary cases we may expect $k$ to execute an essentially uniform precession about the internuclear axis, because of the strong axial field which must result (superposed on a central field) from the presence of two nuclei. The corresponding quantum number $\sigma_k$ represents the component of $k$ along the internuclear axis, and should be subject to the selection rule $\Delta\sigma_k = 0$ or $\pm 1$ (for justification, cf. following section).

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[1] F. Hund, Zeits. f. Physik, **36**, 657 (1926). The notation used here is different from Hund's; his $l$, $i$, and $p$ correspond to $k$, $\sigma$, and $j$ as used here.

By analogy with atomic spectra, Hund assumes that the electric field of the nuclei has no effect on $s$, but that $s$ tends to interact magnetically, as in the atomic case, with $k$. Since $k$ should ordinarily precess rapidly about the internuclear axis, only the component along this axis, namely $\sigma_k$, is effective in orienting $s$. If the interaction between $\sigma_k$ and $s$ is sufficiently intense (case $a$), $s$ is quantized with respect to the internuclear axis, about which it precesses; the corresponding quantum number may be designated $\sigma_s$. By analogy to the rule $\Delta m_s=0$ ($m$=magnetic quantum number) in the Paschen-Back effect in atoms, Hund concludes that $\sigma_s$ should be subject to the rule $\Delta\sigma_s=0$. Since $\sigma=\sigma_k+\sigma_s$, it follows from the selection rules for $\sigma_k$ and for $\sigma_s$ that the rule $\Delta\sigma=0$ or $\pm 1$ should hold.

Hund shows that with a given value of $\sigma_k$, the various possible orientations of $s$ in case ($a$) should give rise to a multiple electron level having (usually[2]) the same number of components as for a multiple atomic level possessing values of $k$ and $s$ equal to those of $\sigma_k$ and $s$ in the present case. Unlike the atomic multiplet, however, the components should all be equally spaced, but the spacing should be of the same order of magnitude as for a similar multiplet in an atom.

If the interaction between $s$ and $\sigma_k$ is small (case $b$), the torque which causes $s$ to follow the motion of the internuclear axis may become inadequate as the rate of nuclear rotation increases. A gradual transition should then occur with increasing $j$, to a condition in which $s$ is oriented and quantized with respect to $j_k$ ($j$=resultant of $j_k$ and $s$), $j_k$ being the resultant of $m$ and $\sigma_k$ (here $\sigma_k=\sigma$). The expected selection rules in the extreme case are $\Delta\sigma_k=0$ or $\pm 1$, $\Delta j_k=0, \pm 1$, and $\Delta j=0, \pm 1$.

Hund also discusses the question of fine structure. For additional details, reference should be made to Hund's paper, and to the excellent discussion by Kemble.[3] In a brief review of the empirical data, Hund presented evidence of good agreement with his theory. One of the main objects of the present paper is to give a more complete discussion of the evidence, including that recently obtained by the writer and given in previous papers of this series and elsewhere.[4,5,6,7]

*Selection rules and intensity relations.* The question of selection rules and intensity relations has been treated only briefly by Hund. For an understanding of the experimentally observed relations in terms of the theory, and of the connection of the Hönl and London-Dennison intensity equations

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[2] Unlike the atomic case, the full number of components corresponding to the multiplicity should always be developed with the $P$ terms; e.g. a $^4P$ term would have four components ($\sigma_k=1$, $\sigma_s=\pm\frac{1}{2}, \pm 1\frac{1}{2}$), instead of three as in the atomic case.

[3] E. C. Kemble, Bulletin of National Research Council Subcommittee on Molecular Spectra, pp. 326–331 and 345–6 (1927).

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

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

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

[7] R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

with Hund's molecular model, a somewhat more detailed consideration is needed. This can be given in terms of the correspondence principle.[8]

Let us begin with a particular harmonic component of frequency $\alpha$,—corresponding to a particular change in the total and azimuthal or other quantum numbers of the electron, and in the nuclear vibrational quantum number,[9]— in the Fourier analysis of the motion of the emitting electron, this harmonic component being taken with reference to a system of axes precessing with the electron orbit about the internuclear axis and of course also following the latter axis in its precession about the axis of total angular momentum. (Strictly, because of the slight perturbation of the orbital motion by the spin $s$, $\alpha$ should be considered as split into a group of components $\alpha \pm \tau\omega_s$, where $\omega_s$ is the frequency of precession of $s$ about the internuclear axis; but, corresponding to the selection rule $\Delta\sigma_s = 0$, the amplitudes of all the components having $\tau > 0$ may be considered negligible). If now we transform to a set of axes fixed in the molecule, one of these being the internuclear or $\sigma$ axis, the previous harmonic component $\alpha$ yields in general only three components (in so far as the precession of $k$ about $\sigma$ is uniform) of frequencies $\alpha$ (linear component along $\sigma$) and $\alpha \pm \omega_\sigma$ (right- and left-handed circular components about $\sigma$). Here $\omega_\sigma$ is the frequency of precession of $k$ about the $\sigma$ axis, and corresponds to the quantum number $\sigma_k$. The three components thus respectively correspond to the transitions $\Delta\sigma_k = 0$ and $\pm 1$. For brevity these three frequencies will be called $\beta^0$, $\beta^+$, and $\beta^-$. The question of the relative amplitudes of these three components need not concern us here.

Now let us consider any one of the above components $\beta$, and let us suppose that we are dealing with Hund's case ($a$). Transforming to a set of axes fixed in space, one axis being in the direction of $j$, we obtain in general three new components, namely a linear component, of frequency $\beta$, along $j$, corresponding to $\Delta j = 0$ ($Q$ branch), and two circular components, of frequencies $\beta \pm \omega_j$, corresponding to $\Delta j = \pm 1$ ($R$ and $P$ branches); $\omega_j$ is the frequency of precession of $\sigma$ about $j$. The relative amplitudes of these components can be expressed as trigonometric functions of the angle $\theta$ whose cosine is $\sigma/j$; this is true even if $\sigma$ differs from $\sigma_k$ because of the presence of $\sigma_s$. The appropriate functions (cf. ref. 7, Eq. 3; the functions given in Eq. 3 are proportional to radiation intensities) are identical in form with those for $\Delta j = 0, \pm 1$ in a line spectrum multiplet, since the Fourier components corresponding to $\Delta\sigma_k = 0, \pm 1$ are identical in form and type (referred to the $\sigma$ axis) with those (referred to the $k$ axis) associated with $\Delta k = 0, \pm 1$ in the atomic case; in the latter case $\cos\theta = (j^2 + k^2 - s^2)/2jk$. (We are here neglecting the effect of molecular vibration,—first pointed out by Kemble; for refs. cf. ref. 7. This alters the amplitude factors somewhat, in the molecu-

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[8] For a detailed discussion of the methods of the correspondence principle, cf. E. Buchwald, "Das Korrespondenzprinzip," F. Vieweg & Sohn, Braunschweig (1923); J. H. Van Vleck, Nat. Res. Council Bulletin No. 54, "Quantum Principles and Line Spectra," Chapter IX (1926); M. Born, "Atommechanik," especially pp. 118–121 (J. Springer, Berlin, 1925).

[9] Cf. A. Kratzer, Naturwiss. **27**, 577 (1923); W. Lenz, Zeits. f. Physik, **25**, 299 (1924); . Condon, Phys. Rev. **28**, 1182 (1926).

lar case.) The identity just stated formed the starting point of Hönl and London's derivations of their equations. In a previous paper[7] it was stated that Hönl and London's three cases (Eqs. 4, 5, 6 of ref. 7) should correspond primarily to $\Delta\sigma_k=0, \pm 1$ rather than to $\Delta\sigma=0, \pm 1$; the reasons for this statement will now be evident from the discussion given above.

In Hund's case (*b*), starting with any one of the three harmonic components $\beta$, we first transform to a set of axes, one of which is along $j_k$, and which precess with $j_k$ about $j$. This gives three components of frequencies $\beta$ and $\beta\pm\omega_{jk}$, which for brevity may be denoted $\gamma^0$, $\gamma^+$, and $\gamma^-$, corresponding to transitions $\Delta j_k=0, \pm 1$. The relative intensities are then given in the same form as before (Eq. 3 of ref. 7); but here $\cos\theta=\sigma_k/j_k$. The next step, using any one of the components $\gamma$, is to transform to axes which are fixed in space and one of which is parallel to $j$. The precession of $j_k$ and $s$ about their resultant $j$ is completely analogous to the precession of $k$ and $s$ about their resultant $j$ in the line spectrum case. Hence the relative intensities for the three components of frequencies $\gamma$, $\gamma\pm\omega_j$, corresponding to $\Delta j=0, \pm 1$, are again given by Eq. (3) of ref. 7, if here $\theta$ is the angle (usually small) between the vectors $j_k$ and $j$, and if $\sigma'-\sigma''$ in Eq. (3) is replaced by $j_k'-j_k''$. By examination of Eqs. (3) it can be seen that if $\cos\theta=1$, all the intensities vanish except those for which $\Delta j=\Delta j_k$; while if $\cos\theta$ is very *near* 1, as is necessarily the case in practise, except for small values of $j_k$ or large values of $s$, the remaining intensities are very small. Except for certain weak series, a rule $\Delta j_s=0$ (where $j_s=j-j_k$) should be obeyed in the case of *doublet* terms, where $j=j_k\pm\frac{1}{2}$.

From the preceding we may conclude that in Hund's case (*b*) the intensity distributions in $P$, $Q$, and $R$ branches (neglecting weak satellite lines where $\Delta j\neq\Delta j_k$) should fall under the same types as in case (*a*), each type being characteristic of a particular combination of values (initial and final) of $\sigma_k$ and $j_k$, in the same way as of the $\sigma$ and $j$ values in case (*a*). Exact equations analogous to the Hönl and London equations will be given for case (*b*) in a subsequent paper. For transition cases between (*a*) and (*b*), it is not yet obvious what the intensity relations should be.

*Singlet electronic states.* The writer has shown that the band spectra of various molecules containing an even number of electrons are naturally classified as corresponding to transitions between singlet electronic states ($^1S$, $^1P$, $^1D$, $\cdots$,) with $\rho\sim 0$ for all and $\sigma=0, 1, 2, \cdots$. The following types of transitions are known (cf ref. 6, Table II): $^1S\rightarrow{}^1S$, $^1S\rightarrow{}^1P$, $^1P\rightarrow{}^1S$, and $^1D\rightarrow{}^1P$. These indicate a selection rule $\Delta\sigma=0, \pm 1$. For the case $\sigma=0$, the rotational states are single, for $\sigma>0$, they are double ("$\sigma$-type doubling"),[5,6] the two rotational states having equal a priori probability.[7] All these relations are in agreement with Hund's theory if we identify $^1S$, $^1P$, and $^1D$ states in the sense here used with the three cases $\sigma_k=0$, 1, and 2 (all with $\sigma_s=s=0$) in Hund's theory. The selection rules $\Delta\sigma_k=0, \pm 1$, $\Delta\sigma_s=0$ are obeyed, and the occurrence of single rotational states for $\sigma=0$ and double rotational states for $\sigma>0$ is also in agreement with Hund's predictions. That $\sigma_k$ (here equal to $\sigma$) is really an electronic quantum number corresponding in general to a precession about the internuclear axis, is supported by the agreement of observed intensity relations,[7] in bands of the types mentioned, with those predicted on the assumption that $\sigma_k$ *is* such a quantum number. To be sure, the evidence in the cases cited gives no ground for decision as to whether it is $\Delta\sigma$ or $\Delta\sigma_k$ which governs the intensities. In many transitions[4,6] of the type $^2P_{1,2}\rightarrow{}^2S$ and $^2S\rightarrow{}^2P_{1,2}$, however, we have $\Delta\sigma_k=\pm 1$, but $\Delta\sigma=\pm\frac{1}{2}$ or $\pm 1\frac{1}{2}$, giving evidence that $\sigma_k$, not $\sigma$, is the real quantum number.

*Doublet electronic states.* Band spectra corresponding to transitions between doublet electronic states are now known for a number of molecules containing an odd number of electrons. While in singlet states Hund's cases (*a*) and (*b*) are not distinguishable, since $s=0$, the two cases should in general be distinct in doublet states, if we suppose that the latter are characterized by $s=\frac{1}{2}$.

For $^2S$ states we then expect $\sigma_k=0$ and $j_k=m$ (Hund's case *b* here becomes identical with his case *d*). Since there is no torque to orient $s$ in the $\sigma$ direction, it might seem that $s$ could orient itself freely in any direction (or with respect to an external magnetic field). But the observed structure of the ZnH and similar bands of a $^2P\rightarrow{}^2S$ type shows that the usual selection rule $\Delta j=0,\ \pm 1$ is observed, and that $\rho=\pm\frac{1}{2}$ for $^2S$ states; also $\sigma=0$ as expected. The definite orientation of $s$ as $\rho$ in $^2S$ states is attributed by Kemble[3] to an interaction between $s$ and a small magnetic field, parallel to $m$, developed by the molecule as a result of its rotation. The slight energy difference ($\rho$-type doubling[5]) which exists, for a given value of $m$, between $F_1$ states ($\rho=+\frac{1}{2}$) and $F_2$ states ($\rho=-\frac{1}{2}$) is also ascribed by Kemble to this field. The observed existence of just two energy levels for each value of $j$ is in agreement with Hund's theory.

In $^2S\rightarrow{}^2S$ transitions,[5,6,10] the observed transitions ($F_1\rightarrow F_1$ and $F_2\rightarrow F_2$) are apparently limited to those in which $\rho$ does not change sign, *i.e.* in which $s$ does not reverse itself. This limitation $\Delta j_s=0$ is in agreement with the theory (cf above under "selection rules" $\cdots$.) for transitions between doublet states which fall under case (*b*). The theory however predicts the existence of additional weak lines, and in particular accounts for the hitherto unexplained (ref. 5, p. 506) apparent existence (ref. 5, p. 489; ref. 10) of an $F_2$ state with $j=0$; a more detailed discussion of the relation of theory to experiment for $^2S\rightarrow{}^2S$ bands will be given in a later paper.

For $^2P$ states, Hund's theory predicts $\sigma_k=1$, with $s=\pm\sigma_s=\frac{1}{2}$ in case (*a*), giving $\sigma=1\frac{1}{2}$ or $\frac{1}{2}$; in case (*b*), $\sigma_k=1$, $s=\frac{1}{2}=\pm j_s$. For many molecules (NO $\beta$ bands,[11] ZnH and other bands listed under $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ in Table II of ref. 6), typical $^2P$ states approximating case (*a*) actually occur, having a double electron level with $\sigma=\frac{1}{2}$ ($^2P_1$) and $\sigma=1\frac{1}{2}$($^2P_2$).

The existence of combinations $^2S\rightarrow{}^2S$, $^2P_{1,2}\rightarrow{}^2S$, $^2S\rightarrow{}^2P_{1,2}$, and $^2P_1\rightarrow{}^2P_1$ and $^2P_2\rightarrow{}^2P_2$ (cf ref. 11, NO $\beta$ bands), indicates that the selection rule

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[10] E. Hulthén, Phys. Rev. **29**, 97 (1927): CaH bands, $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2S$ types.

[11] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. **29**, 211*A* (1927), and forthcoming detailed articles; Nature, **119**, 118 (1927).

$\Delta\sigma_k=0, \pm 1$ is obeyed, while the complete absence of the combinations $^2P_1\rightarrow{}^2P_2$ and $^2P_2\rightarrow{}^2P_1$ in the NO $\beta$ bands gives striking evidence in support of Hund's rule $\Delta\sigma_s=0$. The intensity relations[11] in the NO $\beta$ bands also agree with the theory for case (*a*).

In $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ transitions involving case (*a*) $^2P$ states, neither of the rules $\Delta\sigma_s=0$ and $\Delta j_s=0$ can be observed, since $^2S$ states always fall under case (*b*). Actually in the ZnH, CdH, and HgH bands,[4] we have $+\sigma_s\rightarrow\pm\rho$ in $^2P_2\rightarrow{}^2S$ and $-\sigma_s\rightarrow\pm\rho$ in $^2P_1\rightarrow{}^2S$, [12] giving altogether four *P*, four *Q*, and four *R* branches.

In addition to the more obvious examples of $^2P\rightarrow{}^2S$ and $^2S\rightarrow{}^2P$ transitions, there are several band spectra (CH, OH, MgH, etc.), briefly considered in previous papers,[5,6] which may now likewise be classified as $^2P\rightarrow{}^2S$ (MgH) and $^2S\rightarrow{}^2P$ (CH$\lambda$3900, OH), if one supposes with Mecke[13] that the electronic doublet separation ($^2P_1-{}^2P_2$) shrinks rapidly with increasing *j*. As Hund has shown, this last feature finds a natural explanation in the transition from case (*a*) to case (*b*) of his theory. In this transition $\pm\sigma_s$ should go over, for normal multiplets, according to Kemble (private communication; cf. ref. 26), into $\mp j_s$, resulting in a decreasing electronic energy separation, and in terms of the Kramers and Pauli formula, giving a variable $\sigma$ and $\rho$ (cf Eqs. 1 and 2 below).

Kratzer's interpretation of the CH bands, recently advocated in slightly modified form by the writer,[5] involves, for the final state of the molecule, a constant $\sigma(\sigma=1)$ and $\rho(\rho=\pm\frac{1}{2})$. For very large values of *j* this is obviously in harmony with Hund's case (*b*) as above discussed, for a $^2P$ state. The excellent agreement of the experimental data with Kratzer's interpretation for *small* as well as large values of *j* must now probably be considered fortuitous (in agreement with Mecke and Birge, and contrary to earlier contentions of the writer[5]) in view of the strength of Hund's theory.

Hulthén has recently concluded[10] that certain CaH bands should be classified, like the MgH bands, as $^2P\rightarrow{}^2S$. These differ from the HgH type bands in that the $^2P_2$ states combine only with the $^2S$ states having $\rho=-\frac{1}{2}$, and the $^2P_1$ states only with $\rho=+\frac{1}{2}$, so that there are altogether only two *P*, two *Q*, and two *R* branches. Since in case (*b*) we expect (for normal doublets, $j_s=-\frac{1}{2}$ for $^2P_2$ states and $+\frac{1}{2}$ for $^2P_1$ states, this would indicate that the predicted rule $\Delta j_s=0$ (see above under "selection rules · · · ") is effective here as in $^2S\rightarrow{}^2S$ transitions. The $^2P_1$ and $^2P_2$ states both show *Q* "combination defects" which may be ascribed to $\sigma$-type doubling[14] combined with *Q* "crossing-over,"[15] just as in $^1P\rightarrow{}^1S$ transitions (cf. ref. 6, p. 1205, Eq. (1a), and Fig. 1). In CH$\lambda$3900 there are six branches which follow similar selection rules to the CaH bands. The same is true of the OH

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[12] There are of course two rotational sub-states, for each of the cases $+\sigma_s$ and $-\sigma_s$; in each case one of these combines with $+j_s$, the other with $-j_s$ (cf. ref. 6, Eq. 8*A*.)

[13] R. Mecke, Zeits. f. Physik, **36**, 795 (1926).

[14] The $\sigma$-type doubling appears to be about equally great, in case (*b*), for $^2P_1$ and $^2P_2$ states, judging by the CH and OH bands; in CH (according to Kratzer's analysis) this doubling can be represented by using a double value of *B*.

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

bands, except that there are additional weak branches (satellite series). In these CH and OH bands, or at least in OH, $j_s = +\frac{1}{2}$ for the $^2P_2$ states and $-\frac{1}{2}$ for $^2P_1$, and the $^2P$ doublet is inverted (cf. later paper), but the $\Delta j_s = 0$ rule still holds (for the six strong branches). In CHλ4300 there are twelve branches, but, as will be shown in a later paper, these bands are due to a $^2D \rightarrow {}^2P$ transition. A detailed comparative study of structure and intensity relations for the whole group of $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2P$ transitions will be given in a later paper.

In agreement with Hund's theory, there are in all known $^2P$ states four rotational states for each value of $j$ except for $j = 1$. In case ($a$), this results from $\sigma$-type doubling[15a] in each of the electronic states $^2P_1$ and $^2P_2$. In case ($b$), $\sigma_k$ gives $\sigma$-type doubling,[14] and on this is superposed $\pm s$ doubling; for large values of $j$, the latter goes over into $\rho$-type doubling, since then $j_s \sim \rho$; furthermore, the $\sigma$-type part of the doubling here shows the same properties (cf. above, CaH, CHλ3900, OH) as for typical $\sigma$-type states (e.g. $^1P$ states).[6]

*Triplet electronic states: interpretation of second positive nitrogen and Swan bands.* We now come to the question of band spectra due to combinations of triplet electronic states. For a $^3P$ state, $\sigma_k = 1$, $s = 1$; $^3P_0$, $^3P_1$, and $^3P_2$ correspond in Hund's case ($a$) to $\sigma_s = -1$, 0, and $+1$, respectively, in case ($b$) to $j_s = \pm 1$, 0, $\mp 1$. Hund gives a theoretical diagram (Fig. 4) for a $^3P \rightarrow {}^3P$ transition, and on p. 671–2 makes it probable that the second positive nitrogen bands[16,17,18] are an example of this type corresponding for low values of $j$ to case ($a$) and for high values to case ($b$). The fact that (aside from rotational doubling) only three $P$ and three $R$ branches are known in each band is accounted for by the selection principle $\Delta\sigma_s = 0$, or $\Delta j_k = \Delta j$, limiting the intense transitions to $^3P_0 \rightarrow {}^3P_0$, $^3P_1 \rightarrow {}^3P_1$, and $^3P_2 \rightarrow {}^3P_2$.

For small $j$ values, if case ($a$) holds, the molecular term values should have the form

$$F = F(n) + F(\sigma) + B(j^2 - \sigma^2) + \cdots \tag{1}$$

Here $F(n)$ is the vibrational term, and $F(\sigma)$ is the electronic term which according to Hund's theory should have three equally spaced values cor-

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[15a] The splitting of the rotational levels into two is apparently much more pronounced in $^2P_1$ than in $^2P_2$ states in case ($a$), (ZnH, CdH, HgH, NO, refs. 4, 11); in fact the experimental evidence for any rotational splitting at all in $^2P_2$ states here is confined to certain perturbed lines in the HgH bands (cf. ref. 4, bottom p. 156, and refs. there given).

[16] E. Hulthén and G. Johansson, Arkiv f. Mat., Astron. och Fysik, **18,** No. 28 (1924); Zeits. f. Physik, **26,** 308 (1924). The designations $\alpha$, $\beta$, $\gamma$, $a$, $b$, $c$, are respectively equivalent to $P_3$, $P_2$, $P_1$, $R_3$, $R_2$, $R_1$ in the notation of Lindau and Mecke. When used with numerical subscripts, e.g. $a_3$, the subscript is the value of the quantum designation $m$; the following relations hold,[18a] $P_1$, $R_1$, branches, $j'' = (m + \frac{1}{2}) + 1$; $P_2, R_2$ branches, $j'' = (m + \frac{1}{2})$; $P_3, R_3$, $j'' = (m + \frac{1}{2}) - 1$; thus $(m + \frac{1}{2})$ is the same as $j_k''$ (for values of $j$ sufficiently large so that $j_k$ has a meaning).

[17] P. Zeit, Zeit. Wiss. Photog. **21,** 1 (1921); R. Mecke and P. Lindau, Phys. Zeits., **25,** 277 (1924); P. Lindau, Zeits. f. Physik, **26,** 343; **30,** 187 (1924). Lindau's $m$ values are the same as Hulthén and Johansson's, for the $R$ branch, but one unit lower for the $P$ branch.

[18] R. Mecke, Zeits. f. Physik, **28,** 261 (1924); Phys. Zeits., **25, 1** (1924).

responding to $\sigma=0$, 1, and 2. For large $j$ values, where case (*b*) is approximated, the relation is[1]

$$F=F(n)+F(j,j-j_k)+B(j_k^2-\sigma_k^2)+\cdots. \tag{2}$$

The three values of $F(j,j-j_k)$ should be closer together than those of $F(\sigma)$ in case (*a*), increasingly so with increasing $j$ (cf. Hund's Fig. 3). The arrangement of the band lines and the relation between the $j$ and $j_k$ values for case (*b*) are shown in Fig. 1.

Several features will now be considered which have been discussed only very briefly or not at all by Hund. Since $N_2$ is an even molecule, the $j$ values should (in the writer's numbering) be half-integral. That this is true is shown by an examination of the $\Delta_2F'$ and $\Delta_2F''$ values for small values of $j$; these [14,15] are of the expected form $\Delta_2F=4BT$ with approximately half-integral $T$ values, which shows (cf. ref. 5, p. 491) that the $j$ values are half-integral if Eq. (1) is applicable.

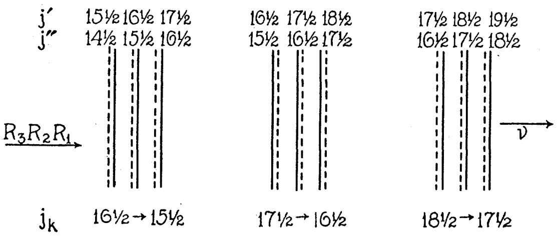

Fig. 1a

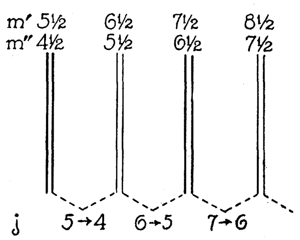

Fig. 1b

Fig. 1*a* corresponds roughly to the arrangement of the lines (missing lines are dotted) in the $R$ branches of the Swan bands.[18a] The arrangement is similar in the second positive nitrogen bands, except that (1) the dotted components are present but weak, (2) the doublets are unresolved in the $R_3$ branches and nearly so in $R_2$ (in regard to the relative positions of the two components in $P_2$ and $R_2$ cf. R. Mecke, ref. 16, p. 271, footnote), (3) $R_1$, $R_2$, and $R_3$ are more widely separated for a given value of $j_k$. The relative position of the strong and weak doublet components in relation to the $j$ values is correct as given, for $N_2$, but has not been definitely determined for the Swan bands. Fig. 1*a* is also applicable to the $P$ branches ($P_1$, $P_2$, $P_3$) if the values of $j'$ and $j'_k$ given are reduced by two units.[18a] Fig. 1*b* shows schematically the arrangement of the strong and weak lines in the $R$ branches in the $N_2^+$ bands, as given by Fassbender.[22]

The question of missing lines has been discussed by Hund. The theoretical values of $j''$ for the first line in each branch are readily specified, noting[18a] that $\sigma=0$ for $P_3$ and $R_3$, 1 for $P_2$ and $R_2$, 2 for $P_1$ and $R_1$, and assigning to $j_{min}$ in each case the first half-integral value in excess of $\sigma$. In Table I the predicted first lines are compared with those observed. The apparent presence of $P_1''$ $(2\frac{1}{2})$ is rather disconcerting. The apparent absence of $R_1'$ $(2\frac{1}{2})$ is less strange, since this component of $R_1$ $(2\frac{1}{2})$ would be weak due to

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[18a] It is possible that the assignment of $\sigma$ values, and the relation of $j$ to $j_k$, for the $P_1R_1$ and $P_3R_3$ branches, should be interchanged in ref. 16, Table I, and Figs. 1a and 2b. Presumably $+\sigma_s$ ($^3P_2$ in case *a*) goes over into $-j_s$ of case *b*, and $-\sigma_s(^3P_0)$ into $+j_s$, for normal triplets, and the reverse for inverted triplets. The relation $(m+\frac{1}{2})=j_k''$ of ref. 16 is reliable.

the alternating intensity phenomenon (see below). On the whole the results are not very satisfactory, but the experimental difficulties in determining the presence or absence of weak lines in a crowded region are great.

TABLE I

*Values of $j''-\frac{1}{2}$ for first recorded line of each branch*

| *Band* | $P_1'$ | $P_1''$ | $P_2$ | $P_3$ | $R_1'$ | $R_1''$ | $R_2$ | $R_3$ |
|---|---|---|---|---|---|---|---|---|
| λ3371 | 3 | 2 | 2 | 1 | 3 | 2 | 2 | 1 |
| 3577 | 3 | 2 | 1 | 1 | 3 | 2 | (1) | 2 |
| 3805 | (3) | 2 | (2) | 1 | (3) | 2 | 1 | 0 |
| 3536 | 3 | 2 | (3) | (3) | (3) | (2) | 2 | 1 |
| 3755 | | | 2 | 1 | | | (2) | 1 |
| 3998 | | | | 1 | | | | 0 |
| 3710 | | | 4 | 1 | | | 4 | 0 |
| 3942 | | | 4 | (1) | 3 | 3 | 2 | (1) |
| Theory | 3 | 3 | 2 | 1 | 2 | 2 | 1 | 0 |

*Notes.* The data for the first five bands are from Hulthén and Johansson,[16] and Zeit.[17]; for the last three, also the presence of $R_3(1)$ in λ3536, the data are according to Lindau.[17] Values in parentheses are uncertain due to superposition.

Closely analogous to the second positive nitrogen bands, as pointed out by Heurlinger, are the Swan (probably $C_2$ or perhaps $C_2H_2$) bands,[19,20] which can therefore probably also be classified as $^3P\rightarrow{}^3P$. The triplet separations in these bands are smaller than in the $N_2$ bands, indicating that Hund's case (*b*) is approached even for rather small $j$ values.

The apparent absence of $Q$ branches in the second positive nitrogen and the Swan bands can be explained by a consideration of the intensity equation of Hönl and London and Dennison for the case $\sigma'=\sigma''$ (cf. ref. 7, Eq. (4)). As in the NO $\beta$ bands,[11] only very short weak $Q$ branches are to be expected (none at all in the case $^3P_0\rightarrow{}^3P_0$), whose presence would probably not be noticed without special search.[21,22] Also, corresponding $P$ and $R$ branches should be approximately equal in intensity;[21] so far as can be seen from the available data,[16] this relation is fulfilled. Since according to Hund's theory $^3P_0$, $^3P_1$, and $^3P_2$ states have equal a priori probability for a given value of $j$, we should furthermore expect $P_1(=P_1'+P_1''$ in Table I$)=P_2=P_3=R_1$ $(=R_1'+R_2'')=R_2=R_3$, approximately. This appears to be not in conflict with the data[16,20] (but cf. Lindau, ref. 17, p. 351).

The rotational doubling in the $N_2$ and Swan bands is presumably $\sigma$-type doubling of the type specified by Eq. (2) of ref. 6.[23] In the Swan bands, the doubling is accompanied by alternate missing lines[19] apparently of the same type as in the $^1D\rightarrow{}^1P$ band of $He_2$ (cf. p. 1208–10 of ref. 6; and cf.

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[19] T. Heurlinger, Dissertation Lund, 1918; R. Komp, Zeits. Wiss. Photog., **10**, 123 (1912); etc.

[20] R. Fortrat, Ann. de physique **3**, 350 (1915): Swan band λ5165. R. C. Johnson, Phil. Trans. Roy. Soc. London, **226A**, 157 (1927): comprehensive summary and large amount of new data.

[21] The Hönl and London equations are of course directly applicable only for case (*a*), but may be expected to be at least qualitatively applicable here, especially for low values of $j$.

[22] Certain additional series in the second positive nitrogen bands have been reported by Konen (cf. Heurlinger, ref. 19, p. 55), but are probably due to impurities (cf. ref. 16).

[23] Mecke earlier interpreted this doubling in the $N_2$ bands as $\rho$-type doubling.[18]

Fig. 1*a* of the present paper with Fig. 3 of ref. 6). This is true for all three *P* branches and all three *R* branches; also, the magnitude of the doublet separations is nearly the same in all three branches of each kind.

Fig. 1*a* shows how the strong and weak doublet components depend on $j$ and $j_k$ in the Swan bands.[18a] It is without doubt significant that the relative positions of the strong and weak components are the same for all three members of a triplet ($P_1$, $P_2$, $P_3$ or $R_1$, $R_2$, $R_3$), hence are determined by $j_k$, not by $j$. For large values of $j$ the $P_2$ and $P_3$ (eventually also the $P_1$) branches draw together (similarly with the *R* branches), and the scale of the multiplicity due to the three orientations of $s$ becomes finer than that of the $\sigma$-type doubling. The tendency seems to be toward a coalescence of $P_1$, $P_2$, $P_3$ and $R_1$, $R_2$, $R_3$ each into a single series of alternate-missing-line *doublets* (of the $He_2$ $^1D \rightarrow {}^1P$ type) whose spacing and intensities are a function of $j_k$, and are presumably characteristic of $\sigma_k$.

The existence of rotational doubling for all three of the electronic states $^3P_0$, $^3P_1$, and $^3P_2$ (in spite of the fact that,—for low values of $j$,—$\sigma$ is zero for $^3P_0$, just as for $^1S$, where rotational doubling is absent) is in agreement with Hund's theory, and gives the latter further support.

In the $N_2$ bands, there is an obvious doubling, accompanied by alternating relative intensities of the two components ($P_1'$ and $P_1''$; and $R_1'$ and $R_2''$), only in the $P_1$ and $R_1$ branches; here the doublet separation is approximately constant ($\Delta\nu \sim 0.24$),[16,17] suggesting that it is mainly "electronic" in origin (cf. ref. 6, bottom of p. 1206). In the $P_2$ and $R_2$ branches, the existence of doubling coupled with alternating intensities is made evident by a displacement of the lines alternately to left and right, together with slight diffuseness in certain lines.[17] In the $P_3$ and $R_3$ branches, the lines form a single series without alternating intensities, but by analogy with the Swan bands, there is no doubt a latent doubling as demanded by the theory; the existence of two series, related in intensity like those in the $P_1$ and $R_1$ branches, but superposed, would account for the observed apparently uniform non-alternating series, while with a truly single series any alternation would necessarily be evident.

*The* NH *bands: note added in proof.*—The NH bands recently analyzed by Hulthén and Nakamura (Nature, Feb. 12, 1927) and classed by them[23a] as $^3P \rightarrow {}^1S$ are in all probability $^3P \rightarrow {}^3S$. The strong *Q* branches show $\Delta\sigma_k \neq 0$. The existence of *Q* combination defects and of three, rather than six, *P* (and *Q*, and *R*) branches show that an *S* electronic state is involved. (The $P'Q'R'$ branches evidently belong to a second band, as Hulthén and Nakamura point out). The *final* states in fact show a narrow triplet separation increasing linearly with $j$, as expected for $^3S$ (case *b*). The initial states, showing wide triplets getting narrower with increasing $j$, must then be $^3P$.

*A generalization concerning alternate suppressed rotational levels.* Alternate weakened or suppressed lines in the $N_2$ and Swan bands, as in the $He_2$ bands (ref. 6, Fig. 2), are presumably due to a partial or complete suppression of alternate *rotational levels*. In the case of $He_2$, it has been shown[6] that the

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[23a] The classification $^3P \rightarrow {}^1S$ was a misprint for $^3P \rightarrow {}^3S$, the writer has since learned from Dr. Hulthén.

observed relations can be explained in terms of a system of missing levels which is characteristic for each type ($^1S$, $^1P$, or $^1D$) of electronic state; the suppression of a level is a function only of $j$ and of $\sigma$; or, since $s=0$ and $\sigma=\sigma_k$ here, we may say that it is a function of $j_k$ and $\sigma_k$. We may say further that, for each of the two types of rotational sub-states in $He_2$, the suppressed values of $(j_k-\sigma_k)$ are characteristic and independent of $\sigma_k$ and of the total quantum number of the excited electron, and are as follows (cf. ref. 6, Fig. 2): $B$ sub-states, $(j_k-\frac{1}{2}-\sigma_k)=0, 2, 4, \cdots$ ; $A$ sub-states, $1, 3, 5, \cdots$ ; note that for $\sigma_k=0$, only $B$ sub-states occur.[6]

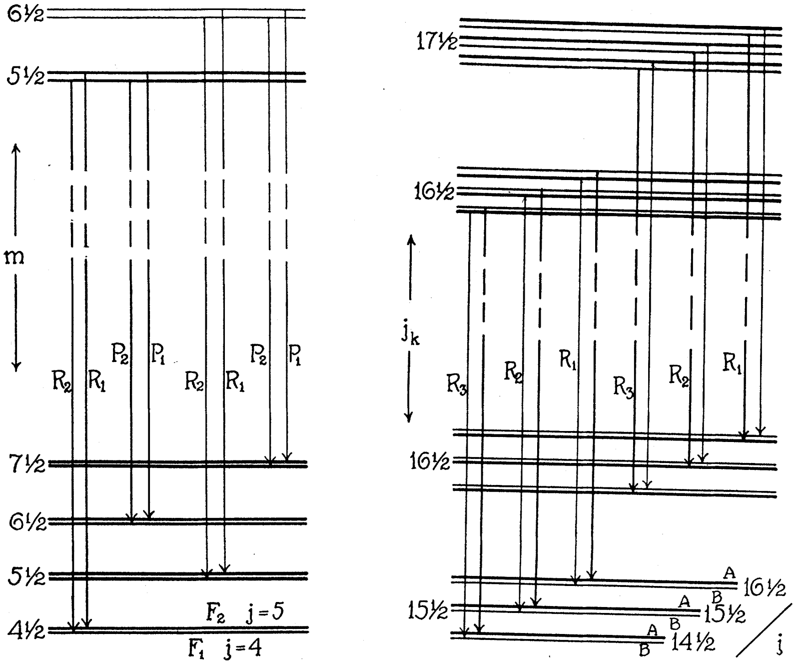

Fig. 2a Fig. 2b

Fig. 2. Possible scheme of rotational energy levels and transitions, (*a*) for the negative nitrogen ($N_2^+$) bands, (*b*) for the Swan and second positive nitrogen bands; in (*b*) the three values of $j(j_k-1, j_k$, and $j_k+1)$ for each value of $j_k$ belong to $^3P_0$, $^3P_1$, and $^3P_2$ levels, respectively.[18a] The spacings and intensities are not to scale. The relative position of the $F_1$ and $F_2$ levels in (*a*) and of the $A$ and $B$ levels in (*b*) is not certain; the same is true in (*b*) of the relative magnitude and order of the $^3P_0$, $^3P_1$, and $^3P_2$ levels and of the $A$ and $B$ rotational levels, in initial and final states. In (*b*), if suitable additional rotational levels are used, $P$ branch transitions can be drawn, similar to the $R$ transitions, with no "crossing over"; $Q$ branch transitions should be very weak and involve crossing over ($A\rightarrow B$ and $B\rightarrow A$), according to Eq. (2) of ref. 6.

Since there seems to be no reason why the scheme of alternate partially or wholly suppressed levels as a function of $j_k$ and $\sigma_k$ should differ from one homopolar molecule to another, it is reasonable to *postulate* that the statement just made for $He_2$ holds exactly for all homopolar molecules. The data on the $N_2$ and Swan bands are evidently compatible with this postulate, since the missing or weakened lines are a function of $j_k$ (not of $j$), hence, we may say ($\sigma_k$ being the same for all three $^3P$ states), of $(j_k-\sigma_k)$. In the

$N_2^+$ bands ($^2S \rightarrow {}^2S$ transition) the two branches ($P$ and $R$) are each composed of alternately strong and weak doublets;[24] here again (Fig. 1b) weakness or strength is determined by $j_k$, or $j_k - \sigma_k$, not by $j$.

In the case of $He_2$, the *absence* of observed combinations, such as $^1P \rightarrow {}^1P$ and $^1S \rightarrow {}^1S$, between like electronic states was attributed[6] to a *complete* suppression of alternate rotational levels in *both initial and final* states. The *occurrence* of the combinations $^3P_0 \rightarrow {}^3P_0$, etc. in the Swan and $N_2$ bands, and $^2S \rightarrow {}^2S$ in the $N_2^+$ bands, then indicates that suppression occurs for one only of the two electronic states (Swan bands) or is only partial ($N_2$ and $N_2^+$ bands); partial suppression might be present in either or both of the two states.

A possible arrangement of the rotational levels for the $N_2$ and Swan bands is shown in Fig. 2b, and for the $N_2^+$ bands in Fig. 2a. In Fig. 2b the three levels corresponding to $^3P_0$, $^3P_1$, and $^3P_2$ are drawn equidistant in accordance with Hund's theory, and in agreement with the observed approximately equal spacing of the triplets formed by $R_1R_2R_3$ or $P_1P_2P_3$. The latter might, however, have arisen from a suitable non-equidistant arrangement of $^3P_0$, $^3P_1$, and $^3P_2$ in initial and final states. It is also uncertain whether the three levels are more widely spaced in the initial or in the final states, and whether in each case $^3P_2$ is the highest level as in a normal multiplet or the lowest as in an inverted multiplet.[18a] The relative magnitude etc. of the rotational doubling in the initial and final states is also uncertain, since the doubling observed in the band-lines represents a difference of two term-doublings. These uncertainties can probably be removed only by the analysis of band systems having terms in common with the bands here under discussion.

*General remarks on term-notation, term-formulation, j values, etc.* Hund's theory gives no explanation of the phenomenon of alternating intensities in band lines.[24a] Also it does not obviously account for the precise nature and selection rules which are observed in $\sigma$-type doubling, although it does predict correctly the presence or absence of such doubling. But at every point where the theory as so far developed is specific, all the experimental evidence appears to be in agreement with it.

The question of a systematic difference between the $j$ numbering of even and odd molecules was not considered by Hund. In terms of the new quantum mechanics, the rotational energy for a $\sigma$-type term is given by $E^m = B[j(j+1) - \sigma^2] + \cdots$.[25] If this formulation is adopted, the experimental evidence[4,5,6,7,11] shows definitely that $j (j = \sigma, \sigma+1, \sigma+2, \cdots)$ is

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[24] M. Fassbender, Zeits. f. Physik, **30**, 73 (1924); R. Mecke, ref. 18.

[24a] W. Heisenberg has recently presented a very interesting theory of alternating intensities (Zeits. f. Physik, Spring, 1927) in terms of the wave mechanics.

[25] This equation, obtained for the symmetrical rotator by D. M. Dennison (Phys. Rev., **28**, 318, 1926), Kronig and Rabi (Nature, **118**, 805 (1926), Phys. Rev. **29**, 262, 1927), and by F. Reiche (Zeits. f. Physik, **39**, 444, 1926), is doubtless also applicable here. Dennison does not decide between integral and half-integral $j$ values, but Kronig and Rabi conclude that only integral values are allowable. This conclusion may well hold when $\sigma$ corresponds to nuclear rotational energy, but in view of the experimental facts, evidently does not hold when $\sigma$ is an electronic quantum number and *when s is present* with a half-integral value.

integral for even molecules and half-integral for odd molecules (the $j$ values in the above formulation are all $\frac{1}{2}$ unit less than those used by the writer in previous papers). The same $j$ values also hold in $\rho$-type terms, and doubtless in general.

In terms of Hund's theory, it is now apparent that the Kramers and Pauli rotational energy term $F(j)=Bm^2+\cdots=2B[(j^2-\sigma^2)^{1/2}-\rho]^2\cdots$, while formally capable of accounting for observed relations, is inappropriate physically, and should be replaced in Hund's cases (*a*) and (*b*) by Eqs. (1) and (2) above; in transition cases, the relation is more complicated. The variable electronic term in Eq. (2), which must also be present in transition cases, probably gives contributions[26] involving all powers of $j$. The contribution to the quadratic term probably accounts for the frequently rather large differences[4,11] between the apparent $B$ values for the components of a $^2P$ or other multiple level; hitherto these have been interpreted as due to (unaccountably large) differences in moments of inertia, but recent work of Kemble and Jenkins[26] indicates that they can be accounted for quantitatively in terms of Hund's theory, with a single moment of inertia. The electronic contribution to the linear term in $j$ also probably accounts in part (not wholly, since secondary $\rho$'s occur even for singlet electronic states) for the frequent occurrence of apparent "secondary $\rho$'s," whose existence is equivalent to the occurrence of a linear term in $j$; also, cf. Kemble, ref. 3, pp. 345–7.

The "effective rotational quantum number" $T$, defined in previous papers[5] as $j-\rho$, retains its meaning in Hund's case *a* (where $\rho=0$, $T=j$). In case (*b*), $T$ might best be redefined as $T=j_k$; in the special case of $^2S$ states (where $j=j_k+\rho$, $\rho=\pm\frac{1}{2}$), this coincides with the previous definition. For transition cases between (*a*) and (*b*), the appropriate definition of $T$ is not evident. When cases *a* and *b* are approximated, Eqs. 8*E*, 13, 14, and 15 of ref. 5, after dropping the terms in $\rho\sigma^2$, remain valid, in terms of $T$, for $F(j)$, $\Delta_1F(j)$, $\Delta_2F(j)$, and $\nu$.

In terms of Hund's theory, it is evident that the notation $^1S$, $^1P$, $^2P$, etc., as used in previous papers of this series, is far from identical in meaning with that for the line spectrum case. According to the theory, the molecular quantities $s$, $\sigma_k$, and $\sigma$ in case (*a*) play the same part in molecular multiplets as do $s$, $k$, and $j$ (Sommerfeld's $j_s$, $j_a$, and $j$) in ordinary atomic multiplets (but cf. ref. 2). The most notable difference is the distinction required between $k$ and $\sigma_k$ in the molecular case. Practically there is at present little evidence on which to base this distinction. Probably $\sigma_k$ is identical with $k$ in many or perhaps even in most of the familiar band spectra. When it becomes possible to determine both $k$ and $\sigma_k$, such a notation as e.g. $^2P_1{}^D$ might be introduced to describe the case $k=2$, $\sigma_k=1$, $s=\frac{1}{2}$, $\sigma_s=-\frac{1}{2}$. In the mean time, the continued use of the simple designations $^2P_1$, $^1S$, etc. would seem to be both appropriate and convenient for the empirical classification of molecular electronic terms.

WASHINGTON SQUARE COLLEGE,
NEW YORK UNIVERSITY,
February 12, 1927.

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[26] E. C. Kemble and F. A. Jenkins, Bull. Am. Phys. Soc. **2**, No. 1, Abstr. No. 9 (Feb. 12, 1927).