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Λ-TYPE DOUBLING AND ELECTRON CONFIGURATIONS IN DIATOMIC MOLECULES

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Abstract

Van Vleck's equations for Λ-type and spin doubling in $^1\Pi$, $^2\Sigma$, and $^2\Pi$ states are restated in convenient form for application to empirical data, explicit equations being given for each component separately in a Λ-type or spin doublet. The equations have been applied to a wide variety of data on many molecules, including data on $^2\Pi$ states corresponding to numerous intermediate coupling cases between *a* and *b*, and have been found to fit excellently (cf. Figs. 1–4). Incidentally this has made possible a revision of the hitherto doubtful assignment of J values for the Q_2 lines in the $^2\Pi$, $^2\Sigma$ bands of CaH, and has permitted identification of the ^SR branch. Empirical values of the coefficients in Van Vleck's equations have been obtained for many molecules, and are given in Tables I and II.

From the observed values of these constants further confirmation of Van Vleck's theoretical results is obtained. In most of the molecules examined a Π and a Σ state are found which stand to each other in the relation called "pure precession" by Van Vleck, or something similar; that is, the Π and the Σ state act as if they had electron configurations essentially alike in all respects except that one electron has $\lambda=0$ in the Σ state but $\lambda=1$ in the Π state, or vice versa. The existence of such relations strongly indicates that the n and l values previously assigned to outer electrons in hydrides have almost the same well-defined significance as they would in an atom formed by *uniting* the H nucleus with the heavier nucleus. For example, in the normal ($^2\Sigma$) and first excited ($^2\Pi$) state of CdH, with configurations $\ldots 5s\sigma^2 5p\sigma$ and $\ldots 5s\sigma^2 5p\pi$, the present evidence shows that the last electron really behaves like a $5p$ atomic electron, even though the normal ($^2\Sigma$) state is formed with a small energy of formation from a normal Cd atom ($\ldots 5s^2$, ^1S) and a normal H atom ($1s$, ^2S). Another type of case, in which a close similarity of the electron orbits to two *separate* atoms is evident, is one which is found in He_2, Li_2, and Na_2. In He_2 the $1s\sigma^2 2p\sigma 3p\sigma$, $^3\Sigma_g^+$ and the $1s\sigma^2 2p\sigma 2p\pi$, $^3\Pi_g$ states act as if the relation of pure precession were fulfilled. This is presumably because the $3p\sigma$ election acts essentially like $2p\sigma$, the $3p\sigma$ and $2p\pi$ both becoming $2p$ on dissociation of the molecule.—In the CaH molecule an interesting complicated case, earlier discussed by Watson, occurs in which strong l-uncoupling and spin uncoupling occur simultaneously in a $^2\Pi$ state. The theory accounts well for the observed relations in this case (Figs. 2, 3, 4).

Introduction

The theory of Λ-type doubling, as developed by Kronig and especially by Van Vleck for $^1\Pi$, $^2\Pi$ and other states of diatomic molecules,[1] has interesting possibilities of application to which not much attention has been given. It is capable of giving helpful clues to the interpretation of band structures and to electron configurations. In a recent paper[2] on the SiH bands, the quali-

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[1] R. de L. Kronig, Zeits. f. Physik 50, 347, 1928 (*singlet states*); J. H. Van Vleck, Phys. Rev. **33,** 467–506 (1929).

[2] R. S. Mulliken, Phys. Rev. **37,** 733 (1931).

tative theory has been used in this way. In the present paper, further qualitative applications of the theory are made, as well as quantitative tests. The closely related theory of spin doubling in $^2\Sigma$ states[1] is also tested and applied. As a result of this work, experimental confirmation of certain details of the theory is obtained,[3] and evidence in regard to the electron configurations of various molecules is secured.

Before proceeding to the application of the theory, it will be helpful to summarize the equations for the widths $\Delta\nu$ of Λ-type doublets in $^1\Pi$ and $^2\Pi$ states and of spin doublets in $^2\Sigma$ states. The equations can be made considerably more useful by giving explicitly the *sign* as well as the magnitude of the $\Delta\nu$'s. This was not done by Van Vleck, although the proper results are contained implicitly in his work.

For Λ-type doubling, the following definition of $\Delta\nu$ (in cm^{-1}) will be used here

$$\Delta\nu_{dc}(J) = T_d(J) - T_c(J). \tag{1}$$

This expression, rather than $T_c(J)-T_d(J)$, has been chosen because it is usually positive. The reasons why $T_d - T_c$ is usually positive, but sometimes negative, form one of the subjects of this paper. The symbol T(term) means E/hc, where E is the total energy. The definitions of c and d rotational levels in Λ-type doubling will be found in a recent article in Reviews of Modern Physics.[4] These definitions were chosen primarily for singlet and case b states, the assignment of the designations c and d for the levels of case a states then being determined on the basis of an adiabatic correlation with case b. This method of assignment for case a seemed advisable because of the many examples of states intermediate between cases a and b, and because of the frequent occurrence of case a states which go over with increasing J into case b. The examples of $^2\Pi$ states discussed below are largely of these types.

For $^2\Sigma$ and also for case b $^2\Pi$ states, the following definition will be used

$$\Delta\nu_{12}(K) = T_1(K) - T_2(K), \tag{2}$$

where $J=K+\frac{1}{2}$ for T_1 and $J=K-\frac{1}{2}$ for T_2.

REVIEW OF THEORETICAL RELATIONS FOR $^1\Pi$ AND OTHER CASE b Π STATES

For any $^1\Pi$ state, Van Vleck finds[5,6]

$$\begin{aligned} T_d(K) &= T_0 + B_vK(K+1) - 2C + (C + C_1)K(K+1) + \cdots; \\ T_c(K) &= T_0 + B_vK(K+1) - 2C + (C + C_2)K(K+1) + \cdots. \end{aligned} \tag{3}$$

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[3] The main features of the theory are in striking agreement with experiment.[1]

[4] For definitions of c and d levels in Λ-type doubling, of positive and negative rotational levels, of Σ^+ and Σ^- states, and of even and odd (g and u) electronic states, cf. R. S. Mulliken, Rev. Modern Physics, **3**, 91–95 and 146–7 (1931).

[5] Cf. Eq. (44) of Ref. 1. Here we have used K instead of J (Van Vleck's j), which is permissible since $K\equiv J$ in singlet states. The correlation of the component involving C_1 with T_d is not given explicitly in Van Vleck's paper, but can be seen by a study of the development given there, according to a private communication from Van Vleck.

[6] All coefficients such as C, C_1 and quantities such as ν, $\Delta\nu$, are given here in spectroscopic units (cm^{-1}), although in Van Vleck's paper C, C_1, etc. are in ergs and ν is in sec.^{-1}

Hence, as was also shown by Kronig,[1]

$$\Delta\nu_{dc}(K) = qK(K+1), \text{with } q = C_1 - C_2. \tag{4}$$

In Eqs. (3) and (4), C and C_2 may be expected usually to be much smaller than C_1. These coefficients are given[7] by

$$\begin{aligned} C &= -4\Sigma_{(\text{all } v \text{ values of all } {}^1\Delta \text{ states})} \left| BL_y(\Delta, \Pi) \right|^2/\nu(\Delta, \Pi), \\ C_1 &= 8\Sigma_{(\text{all } v \text{ values of of all } {}^1\Sigma^+ \text{ states})} \left| BL_y(\Pi, \Sigma^+) \right|^2/\nu(\Pi, \Sigma^+), \end{aligned} \tag{5}$$

while C_2 is like C_1 except that the summation is over all ${}^1\Sigma^-$ states.[4] [In the case of a molecule composed of two atoms of the same element, the summations need be taken only over ${}^1\Delta_g$ and ${}^1\Sigma_g$ states if the ${}^1\Pi$ is a ${}^1\Pi_g$, or over ${}^1\Delta_u$ and ${}^1\Sigma_u$ states if it is ${}^1\Pi_u$.] In these equations $\nu(\Pi, \Sigma^+)$ is the frequency (cm^{-1}) corresponding to any ${}^1\Pi \rightarrow {}^1\Sigma^+$ transition from the given ${}^1\Pi$ state and v value to any ${}^1\Sigma^+$ state and v value, and is taken as positive or negative according as the ${}^1\Pi$ level is above or below the ${}^1\Sigma^+$ level; $\nu(\Delta, \Pi)$ has an analogous meaning. The expression $BL_y(\Pi, \Sigma^+)$ denotes the matrix component, corresponding to a ${}^1\Pi$, ${}^1\Sigma^+$ transition involving the given ${}^1\Pi$ state, of the quantity BL_y, B being $h/8\pi^2\mu c r^2$ and L_y being one of the components L_x and L_y of the resultant electronic orbital angular momentum vector L perpendicular to the electric axis (the component parallel to the axis is represented by the quantum number Λ). Approximately, at least if v is small in the Π state, B can be treated as a constant (equal to B_v of the Π state), and the summation over different v values in each Σ^+ or Δ state in Eqs. (5) can be set equal to unity. This gives[8]

$$C_1 \sim 8B_v{}^2\Sigma_{(\text{all } {}^1\Sigma^+ \text{ states})} \left| L_y(\Pi, \Sigma^+) \right|^2/\nu(\Pi, \Sigma^+), \tag{5a}$$

with corresponding equations for C and C_2. In Eq. (5a), $\nu(\Pi, \Sigma^+)$ should be a suitably weighted mean of the ν's which would correspond to transitions between the given Π level with its given v to various v values of the Σ^+ state. (This means ν can be determined in the manner described below in the first paragraph of "calculation of p_0, q_0, and γ_0 for pure precession.") If the interaction between spin (S) and orbital electronic motion is very small, as in Hund's case b, the results just given for ${}^1\Pi$ and ${}^1\Sigma$ states obviously apply also to Π and Σ states in general.

In the summations given for C_1 or C_2 (let us assume for the moment that $C \sim 0$), it often happens that one term is much larger than all the rest because ν is unusually small or because the BL_y matrix component is much larger for one ${}^1\Sigma$ state than for all the rest. If one matrix component predominates over all others, we have Van Vleck's case of **"pure precession,"** or something similar to it. In this case we may sometimes think of L as precessing uniformly and corresponding to a well-defined quantum number. The ${}^1\Pi$ and

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[7] Cf. Eq. (45) of Ref. 1. L_y (same as Van Vleck's l_y) is used here, since it is identical for singlet states with Van Vleck's P_y (y component of total electronic angular momentum), and since L_y rather than P_y is needed in equations for ${}^2\Pi$ states (cf. Eqs. 9, 10). The arguments of BL_y and of ν have been abbreviated here in a way that is used by Van Vleck later in his paper, but which is also convenient for ${}^1\Pi$ states.

[8] Cf. pp. 478–9, Eqs. (23)–(24), footnote 39, and p. 488 of Ref. 1.

the corresponding ${}^1\Sigma$ state then share this L and differ only in that $\Lambda=1$ for ${}^1\Pi$ and $\Lambda=0$ for ${}^1\Sigma$. But usually matters are more complicated, so that we should not think of L as being a well-defined quantum number for the molecule as a whole. The case of pure precession can, however, still be fulfilled if even just one electron has a well-defined l. If the sum of the λ values for all other electrons is zero, then Λ is equal to the λ value of this one electron. If this special electron has $l=1$, then according as it has $\lambda=1$ or 0, we have a ${}^1\Pi$ or a ${}^1\Sigma$ state; and we have a relatively very large matrix component for $BL_y(\Pi, \Sigma)$ in Eq. (5) or (5a). Similarly if it has $l=2$, we have a ${}^1\Delta$, a ${}^1\Pi$, and a ${}^1\Sigma$ state, for which $L_y(\Delta, \Pi)$ and $L_y(\Pi, \Sigma)$ are both large, and C is comparable with C_1. When more than one electron has pure precession, similar but more complicated cases are also possible.

The existence of well-defined l's is to be expected in the case of outer electrons whose orbits approximate those in the atom which would be obtained by uniting the two nuclei. This situation occurs especially in the case of hydrides where the charge on the H nucleus is much smaller than the effective charge on the other nucleus, and (for one electron) in excited states of such molecules as H_2 and He_2, where the orbit-dimensions of the excited electron greatly exceed the distance between the nuclei. As will be shown later, Λ-type doubling relations indicating well-defined l's are also found for electrons whose orbits are nearly the same as if the two atoms were separate, and we again have a case which will here be classified under the heading "pure precession," although it is not the same as Van Vleck's pure precession.

If the case of pure precession applies approximately to an electron which determines Λ, all other electrons being in closed shells (or else one or more of them in σ orbits differing in l or n from the precession electron), then[9]

$$C = -B_v^2(l^2+l-2)/\nu(\Delta, \Pi), \text{ and } C_1 = 2B_v^2 l(l+1)/\nu(\Pi, \Sigma), \tag{6}$$

while $C_2=0$, since the conditions stated just before Eqs. (6) can be fulfilled only for Σ^+ states. If $l=1$, of course $C=0$. For any value of l, Eq. (6) gives for q of Eq. (4),

$$q = 2B_v^2 l(l+1)/\nu(\Pi, \Sigma) \tag{7}$$

Eqs. (6) and (7) would also apply, with L instead of l, in case L should be a well-defined quantum number. In this case, Σ^- as well as Σ^+ states are possible. If the Σ state is Σ^-, we have $C_1=0$, while C_2 is given by the second part of Eq. (6) and the expression for q in Eq. (7) must be preceded by a minus sign. Eqs. (6) and (7) involve the assumption that B_v is independent of Λ for the states concerned in the pure precession.[9] This is to be expected only in the *ideal* case of pure precession. When it is not true, the correct procedure would seem to be to use B_v of the Π state in Eqs. (6) and (7), and then for $\nu(\Pi, \Sigma)$ to use the value which would be obtained if B_v were the

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[9] Cf. Ref. 1, Eq. (46) and pp. 488–9. Professor Van Vleck kindly pointed out to us the necessity of modifying Eqs. (6) and (7) when there is independent precession of l's of more than one electron of given n and l. The argument leading up to Eq. (7a) was also suggested by him.

same for the Σ as for the Π state (cf. later section,—p109,—on "calculation of p_0, q_0, and γ_0 for pure precession").

According to the conditions stated in introducing Eq. (6), Eqs. (6) and (7) are applicable to pairs of states such as the following: $(A)np\sigma$, ${}^2\Sigma^+$ and case b $(A)np\pi$, ${}^2\Pi$; $(A)(m\sigma)(np\sigma)$, ${}^1\Sigma^+$ and $(A)(m\sigma)(np\pi)$, ${}^1\Pi$. Often, however, we have cases such as the following, with two, three, or more electrons alike in n and l: $(A)np\sigma^2$, ${}^1\Sigma^+$ and $(A)np\sigma np\pi$, ${}^1\Pi$; $(A)np\sigma^2np\pi$, ${}^2\Pi$ and $(A)np\sigma np\pi^2$, ${}^2\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Delta$, ${}^4\Sigma^-$, and $np\pi^3$, ${}^2\Pi$; and so on. In the case of *two* electrons alike in n and l, and giving a ${}^1\Sigma^+$ state (σ^2) and a ${}^1\Pi$ state ($\sigma\pi$), it is easily shown that in the limiting case of *independent* pure precession of their l's (and approximately in the actual case, unless there is a well-defined L), the values of C_1 and q are just *twice* those given by Eqs. (6) and (7). The proof is as follows.[9] Suppose we designate by $l_y(\sigma, \pi)$ the value of the l_y matrix element which one gets in Eq. (5a) for pure precession for the case of a single electron fulfilling the conditions stated before Eq. (6). Suppose further that we designate by $l_y(\sigma^2, \sigma\pi)$ the corresponding matrix element for the above case of two electrons alike in n and l. Letting ψ_0 and ψ_1 represent wave-functions, neglecting spin, corresponding respectively to the two cases $\lambda=0$ and $\lambda=1$ (σ and π), we have

$$l_y(\sigma, \pi) = \int l_y\psi_0\psi_1^* d\tau,$$

$$l_y(\sigma^2, \sigma\pi) = \int (l_{y_1}+l_{y_2})[\psi_0(1)\psi_0(2)](1/2^{1/2})[\psi_0(1)\psi_1(2)+\psi_0(2)\psi_1(1)]^* d\tau_1 d\tau_2.$$

The second relation is true on the assumption of a vanishingly small interaction between the two electrons, but should usually hold fairly well in the actual case, unless there is a well-defined L. The integral reduces to $(1/2^{1/2})[\int l_{y_1}\psi_0(1)\psi_1^*(1)d\tau_1+\int l_{y_2}\psi_0(2)\psi_1^*(2)d\tau_2]$, which is $2/2^{1/2}$ times the integral representing $l_y(\sigma, \pi)$. Hence $|l_y(\sigma^2, \sigma\pi)|^2=2|l_y(\sigma, \pi)|^2$. From this the statement above as to the values of C_1 and q follows. That is:

$$(\sigma^2, \sigma\pi): q = 4B_v{}^2l(l+1)/\nu(\Pi, \Sigma) = C_1. \tag{7a}$$

In cases where the number of electrons with given n and l is greater than one or two, more complicated relations may in general be expected. If, however, the Σ and Π states have respectively the configurations $\sigma\pi^4$ and $\sigma^2\pi^3$ (closed shells *minus* one σ or π electron), it is fairly evident that Eqs. (6) and (7) apply just as to the case where only one σ or π electron is *present* outside of closed groups.

${}^1\Sigma$ *states.* In connection with Eqs. (3), (5), (5a), (6), the following equation for ${}^1\Sigma$ states is of interest.[10]

$$T(K) = T_0 + B^*K(K+1) + \cdots,$$

where

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[10] This is obtained from the equation for ${}^2\Sigma$ states (Eq. 15 below) by dropping the terms in the latter which depend on electron spin.

$$B^* = B_v - 8\Sigma_{(\text{all } {}^1\Pi \text{ states})} \left| BL_y(\Pi, \Sigma) \right|^2 / \nu(\Pi, \Sigma) \tag{8}$$

In the case of pure precession, the summation in Eq. (8), like C_1 or C_2 of Eq. (5), becomes identical with C_1, or with C_2, in the case of a Σ^- state, of Eq. (6).

REVIEW OF THEORETICAL RELATIONS IN $^2\Pi$ AND $^2\Sigma$ STATES

For the general intermediate case between *a* and *b* Van Vleck obtains for $^2\Pi$ states an equation for the term values that includes the effects of spin doubling and Λ-type doubling simultaneously. Van Vleck's equation, which involves an expansion that gives a good approximation if $|A| << |\nu(\Pi, \Sigma)|$, is as follows:[11]

$$\begin{aligned} T(J) = T_0 &+ B_v\{(J+\tfrac{1}{2})^2 - 1 \pm \tfrac{1}{2}X\} + \tfrac{1}{2}\{o + \tfrac{1}{2}p^* + q^*(J+\tfrac{1}{2})^2\} \\ &\pm \tfrac{1}{2}X^{-1}\{(2-Y)(o + \tfrac{1}{2}p^* + q^*) + (p^* + 2q^*)(J-\tfrac{1}{2})(J+3/2)\} \\ &+ [\pm]\tfrac{1}{2}(J+\tfrac{1}{2})\{[\pm 1 + X^{-1}(2-Y)](\tfrac{1}{2}p + q) \\ &+ 2X^{-1}q(J-\tfrac{1}{2})(J+3/2)\} + \cdots . \end{aligned} \tag{9}$$

The first term $T_0 + B_v\ \{\cdots\}$ in Eq. (9) is nothing other than the familiar Hill and Van Vleck term, which correctly represents the energy, taking care of the effects of spin uncoupling, in the absence of *l*-uncoupling. The latter, which is the cause of Λ-type doubling, gives rise to the remaining terms in Eq. (9). In Eq. (9) the upper (+) sign in the case of a ± sign refers to T_2 levels, the lower (−) sign to T_1 levels, except that in the case of the *bracketed* [±] sign, the + sign refers to T_d levels, the − sign to T_c levels. It will be seen that Eq. (9) really contains equations for all of the four kinds of levels T_{2d}, T_{2c}, T_{1d}, and T_{1c}. [It should be recalled that T_2 corresponds to $^2\Pi_{1\frac{1}{2}}$ in regular case *a*, to $J = K - \frac{1}{2}$ in case *b*, and to $^2\Pi_{\frac{1}{2}}$ in inverted case *a*, while T_1 corresponds to $^2\Pi_{\frac{1}{2}}$ in regular case *a*, to $J = K + \frac{1}{2}$ in case *b*, and to $^2\Pi_{1\frac{1}{2}}$ in inverted case *a*.] In Eq. (9), X stands for the *positive square root* of $[Y(Y-4) + (J+\frac{1}{2})^2]$, with $Y = A/B_v$, where A is the coefficient of the coupling energy between S and the orbital electronic motion.

The coefficient q in Eq. (9) has exactly the same meaning as in Eqs. (4)–(5), except of course that $^2\Sigma$, $^2\Pi$ are meant here instead of $^1\Sigma$, $^1\Pi$; q^* stands for $C_1 + C_2 = q + 2C_2$. The coefficient p^* means $a_1 + a_2 = p + 2a_2$, while p is given by

$$p = a_1 - a_2, \tag{10}$$

where

$$a_1 = 8\Sigma_{(\text{all } v \text{ values of all } {}^2\Sigma^+ \text{ states})} [1/\nu(\Pi, \Sigma^+)] \\ \{(\text{Real part of } [AL_y(\Pi, \Sigma^+) BL_y(\Sigma^+, \Pi)]\}, \tag{10a}$$

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[11] Eq. (9) is obtained from Van Vleck's Eq. (61) as follows. First μ, μ^*, η, etc. in Eq. (61) of Ref. 1 are replaced according to Van Vleck's Eqs. (58). In doing this, each μ has a double value ($\mu = \theta \pm \zeta$), which gives Λ-type doubling. On investigation, it proves that $\mu = \theta + \zeta$ has to be associated with the *d* levels when there is a + sign (T_2) in Eq. (61), but with the *c* levels when there is a − sign (T_1) in Eq. (61), i.e. $\mu = \theta + \zeta$ corresponds to T_{2d}, and T_{1c}. Similarly, $\mu = \theta - \zeta$ corresponds to T_{2c}, and T_{1d}. When due account is taken of the ± signs which give T_1 or T_2, and of those which give T_c or T_d, and when suitable abbreviations are introduced, Eq. (9) results.

with a corresponding summation, involving ${}^2\Sigma^-$ states, for a_2. The coefficient o in Eq. (9) is given by

$$o = \Sigma_{(\text{all } v \text{ values of all } {}^2\Sigma \text{ states})}\left[1/\nu(\Pi, \Sigma)\right] \left| AL_y(\Pi, \Sigma) \right|^2. \tag{11}$$

[In case the molecule is composed of two atoms of the same element, the summations for a_1, a_2, or o need be taken only over ${}^2\Sigma_g$ or only over ${}^2\Sigma_u$ states, according as the ${}^2\Pi$ state is ${}^2\Pi_g$ or ${}^2\Pi_u$.]

It should be pointed out that Eq. (9) was derived[1] under the assumption that interactions of the ${}^2\Pi$ state under consideration with ${}^2\Delta$ states are negligible in comparison with interactions with ${}^2\Sigma$ states. This is usually but by no means always true: cf. Eqs. (3), where the interactions with ${}^1\Delta$ states are taken care of by the terms involving C. To remedy this deficiency, further terms should be added to Eq. (9), but the form of these is not yet known. Another deficiency in Eq. (9) is the fact that it takes no account of the variation of the moment of inertia of a molecule with J. This can be removed probably nearly perfectly by replacing B_v wherever it appears, explicitly or (in Y, X, o, p, and q) implicitly, by $B_{v,\,\kappa}$ as given by Eqs. (24) ahead.

In the same way that Eq. (5a) was obtained as an approximation to Eq. (5), one gets

$$a_1 \sim 8AB_v\Sigma_{(\text{all } {}^2\Sigma^+ \text{ states})} \left| L_y(\Pi, \Sigma^+) \right|^2/\nu(\Pi, \Sigma^+). \tag{10b}$$

If we have approximately the case of "pure precession," the expressions for q and p can be simplified, giving

$$q = 2B_v^2 l(l+1)/\nu(\Pi, \Sigma),\ p = 2AB_v l(l+1)/\nu(\Pi, \Sigma) \tag{12}$$

Eqs. (12) hold under the same provisos as Eqs. (6) and (7) and apply only for Σ^+ states. If there is pure precession of an L, this should appear instead of l in Eq. (12). With an L, the Σ state may be Σ^-, and in this case a minus sign must be inserted on the right side of each Eq. (12). Under the provisos which apply to Eq. (7a), the right hand side of each Eq. (12) must be multiplied by a factor 2 (cf. Eqs. 7 and 7a).

If one puts $A \sim +\infty$ or $-\infty$ in Eq. (9), one gets for $A \sim +\infty$ in the T_1 case and for $A \sim -\infty$ in the T_2 case, corresponding respectively to regular and inverted ${}^2\Pi_{\frac{1}{2}}$, equations which can be written as follows:

$$T(J) = \text{Const.} + B_v J(J+1) \mp [\pm]\tfrac{1}{2}p(J+\tfrac{1}{2}) + \cdots. \tag{13}$$

The upper sign in $\mp$ applies when A is positive, the lower when it is negative, while the upper sign in $[\pm]$ applies to T_d, the lower to T_c. The constant is different for A positive than for A negative. Eq. (13) shows that in case a ${}^2\Pi_{\frac{1}{2}}$ states, the correction terms corresponding to Λ-type doubling are practically equal and opposite for $T_c(J)$ and $T_d(J)$.

Experimentally it is easier to study the doublet separations $\Delta\nu_{dc}$ than the terms themselves. From Eq. (9) the following expression can be obtained immediately (cf. Eq. 1):

$$\Delta\nu_{dc}(J) = [(\tfrac{1}{2}p+q)(\pm 1 + 2X^{-1} - YX^{-1}) + 2qX^{-1}(J-\tfrac{1}{2})(J+3/2)](J+\tfrac{1}{2}) \tag{14}$$

In Eq. (14) the + sign in ± 1 refers to T_2 levels, the − sign to T_1 levels. For case a $^2\Pi_{\frac{1}{2}}$ states this reduces (cf. Eq. 13) to

$$\text{Case } a\ {}^2\Pi_{\frac{1}{2}}\!: \Delta\nu_{dc} = \pm\, p(J+\tfrac{1}{2}) + \cdots. \tag{14a}$$

Here the − sign applies when A is positive, the + when it is negative.

If in Eq. (14) we put $A \sim -\infty$ in the T_2 case or $A \sim +\infty$ in the T_1 case, and suitably expand, both results can be expressed[12] by

$$\text{Case } a\ {}^2\Pi_{1\frac{1}{2}}\!: \Delta\nu_{dc} = \pm\, (p/Y^2 + 2q/Y)(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+3/2) + \cdots, \tag{14b}$$

the + sign applying when A is positive, the − sign when it is negative. [The *term* equations for $^2\Pi_{1\frac{1}{2}}$, analogous to Eq. (13) for $^2\Pi_{\frac{1}{2}}$, are more complicated and less interesting, and so are not given here.]

In real case $a(|Y|>>1$, but not infinite), Eq. (14a) gives wide Λ-type doublets, since p is approximately proportional (cf. Eq. 12) to $AB_v = B_v^2 Y$, while Eq. (14b) gives narrow doublets, since $(p/Y^2 + 2q/Y)$ is approximately proportional to $B_v^3/A = B_v^2/Y$ (cf. Eqs. 12, 10, 10a). Since p (and so p/Y^2) may be expected to have practically always the same sign as $2q/Y$ (cf. Eqs. 4, 5, 5a, 10, 10a, 10b) for a given $^2\Pi$ state, Eqs. (14a) and (14b) show that $\Delta\nu_{dc}$ should practically always have opposite signs for a $^2\Pi_{\frac{1}{2}}$ and its corresponding $^2\Pi_{1\frac{1}{2}}$ state in case a. In practice, $\Delta\nu_{dc}$ is commonly negative for $^2\Pi_{\frac{1}{2}}$ in case a and positive for $^2\Pi_{1\frac{1}{2}}$; the reasons for this will be discussed shortly. A study of the behavior of Eq. (14) shows that, for states which are near case a for low J values but go over to case b with increasing J, $\Delta\nu_{dc}$ finally changes sign in the case of the $^2\Pi_{\frac{1}{2}}$ levels (cf. Fig. 1). Thus for large enough J it has the same sign for T_1 and T_2 levels, as is required in case b.

Spin doubling in $^2\Sigma$ states. For $^2\Sigma$ states, Van Vleck finds[13]

$$T = T_0 + O + B^*K(K+1) + \tfrac{1}{2}\gamma[J(J+1) - K(K+1) - S(S+1)] + \cdots, \tag{15}$$

where of course $S=\frac{1}{2}$. In Eq. (15),

$$\left.\begin{aligned} O &= -\Sigma_{(\text{all }^2\Pi\text{ states})}[|AL_y(\Pi,\Sigma)|^2/\nu(\Pi,\Sigma)], \\ B^* &= B_v - 8\Sigma_{(\text{all }^2\Pi\text{ states})}[|BL_y(\Pi,\Sigma)|^2/\nu(\Pi,\Sigma)], \end{aligned}\right\} \tag{16}$$

$$\text{and } \gamma = 8\Sigma_{(\text{all }^2\Pi\text{ states})}[1/\nu(\Pi,\Sigma)]\{\text{Real part of }[AL_y(\Pi,\Sigma)BL_y(\Sigma,\Pi)]\} \tag{17}$$

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[12] The equation given here for case a $^2\Pi_{\frac{1}{2}}$ is the same, except for the precise specification of the sign, as the equation given by Van Vleck (cf. Ref. 1, Eqs. 49, 56). Eq. (14b) corresponds to Van Vleck's Eqs. (50, 51), $-2q/|Y|$ here corresponds to Van Vleck's b,— except that Eq. (14b) contains a term $p/Y|Y|$ neglected by Van Vleck. Actually this term is of the same order of magnitude as the term $2q/|Y|$, as can be seen by considering the case of pure precession (Eq. 12 above), and remembering that $Y=A/B$.

[13] Eq. (15) is easily obtained from Van Vleck's Eq. (65),— cf. his Eq. (67),—by amalgamating the terms $-(1/4)\gamma \pm \frac{1}{2}h\Delta\nu$, with the + sign for $J=K-\frac{1}{2}$; hcT_0 is the same as Van Vleck's E. Here we have defined γ so that it is the *negative* of Van Vleck's a'. As Van Vleck remarks, γ in Eqs. (15) and (18) should really be replaced by $\gamma + a''$, where $\frac{1}{2}a''\,[J(J+1) - K(K+1) - S(S+1)]$ is the energy of the spin S in the magnetic field produced by the rotation of the nuclei. Van Vleck states that a'' is of the order of m/μ times the coefficient A (m and μ are respectively the electronic mass and the reduced mass of the nuclei), and shows that one then expects $|a''| < |\gamma|$. Although it would be difficult to prove, it seems probable that a'' is usually negligible compared with γ, and we shall so assume in this paper.

[In case the molecule is composed of two atoms of the same element, the summations need be taken only over all $^2\Pi_g$ or over all $^2\Pi_u$ states, according as the $^2\Sigma$ state is $^2\Sigma_g$ or $^2\Sigma_u$.] From Eq. (15) one finds (cf. Eq. 2),

$$\Delta\nu_{12}(K) = \gamma(K + \tfrac{1}{2}). \tag{18}$$

If for a particular $^2\Sigma$ and $^2\Pi$ state the case of "pure precession" holds, then, at least if the provisos applying to Eqs. (6) and (7) are fulfilled, the summation for γ in Eq. (18) reduces to a single term, and this one term becomes identical, if B_v is the same for two states, with the single term to which the summation for p reduces. Since $p = a_1 - a_2$, and since $a_2 = 0$ for Σ^+ states, this single term is one of the terms of a_1 (cf. Eq. (10a)). In this case (cf. Eq. (12)) we have

$$\gamma = p = 2AB_v l(l + 1)/\nu(\Pi, \Sigma) \tag{19}$$

At the same time, O of Eqs. (15), (16) becomes equal to $-o$ of Eqs. (9), (11), and $B^* - B_v$ to q of Eq. (9).

Spin doubling at high J in $^2\Pi$ states. If A is not too large, the rotational levels of a $^2\Pi$ state become approximately of case b type when J is large enough. It is of interest to consider the form of the doublet separation $\Delta\nu_{12}(K)$ for this case. $\Delta\nu_{12}(K)$ can be obtained here by taking $T_1(K) - T_2(K) = T_1(J_1) - T_2(J_2)$, where $J_1 = K + \frac{1}{2}$ and $J_2 = K - \frac{1}{2}$. If the Λ-type doubling is negligible, we need only the Hill and Van Vleck formula,—the term $T_0 + B_v\{\cdots\}$ in Eq. (9),—and from this get

$$HVV, \Delta\nu_{12}(K) = B_v[(2K + 1) - \tfrac{1}{2}(X_1 + X_2)], \tag{20a}$$

where

$$X_1 = X(J_1) = [Y(Y - 4) + 4(K + 1)^2]^{1/2}, \text{ and}$$
$$X_2 = X(J_2) = [Y(Y - 4) + 4K^2]^{1/2}.$$

Often, however, the effects of Λ-type doubling are not negligible. Using the complete Eq. (9) to get $\Delta\nu_{12}(K)$, one obtains for the case that $8K^2 >> Y^2$, after a considerable amount of algebraic manipulation including an expansion, the following simple approximate relation:

$$\Delta\nu_{12}(K) = [HVV, \Delta\nu_{12}(K)] - \tfrac{1}{2}(p^* \pm p)(K + \tfrac{1}{2}) + \cdots, \tag{20b}$$

where the $+$ sign in $\pm$ refers to the d levels, the $-$ sign to the c levels. Recalling that $p^* = a_1 + a_2$, $p = a_1 - a_2$, we find that if the $^2\Pi$ state interacts mainly only with one or more $^2\Sigma^+$ states, so that $a_2 = 0$ (cf. Eq. 10a), we have $p^* = p$, and

$$\Delta\nu_{12c}(K) = [HVV, \Delta\nu_{12}(K)] + \cdots, \tag{20c}$$

$$\Delta\nu_{12d}(K) = [HVV, \Delta\nu_{12}(K)] - p(K + \tfrac{1}{2}) + \cdots. \tag{20d}$$

If the interaction is mainly with $^2\Sigma^-$ states, we have $a_1 = 0$ and the left-hand sides of Eqs. (20c) and (20d) should be interchanged. As will be shown later in this paper, the condition that the $^2\Pi$ state interacts mainly only with $^2\Sigma^+$ or with $^2\Sigma^-$ states—in fact mainly with just *one* $^2\Sigma$ state, usually a $^2\Sigma^+$ state,—seems to be practically always fulfilled.

Hence it is to be expected that, for sufficiently large K values, $\Delta\nu_{12}(K)$ will usually be given by the Hill and Van Vleck equation (20a) for the c rotational levels, but will *differ* from this for the d rotational levels approximately by the amount $-p(K+\frac{1}{2})$. This last quantity, it will be noted, is essentially the same as $\Delta\nu_{dc}$ of regular case a $^2\Pi_{\frac{1}{2}}$. In the case of pure precession involving the $^2\Pi$ and a $^2\Sigma^+$ state, a case which is usually closely approximated, the quantity $-p(K+\frac{1}{2})$ is exactly the same, except for sign, as the quantity $\gamma(K+\frac{1}{2})$ which gives $\Delta\nu_{12}(K)$ for the $^2\Sigma$ state (cf. Eqs. 18, 19).

The relations stated in the preceding paragraph, which hold when there is pure precession between a $^2\Pi$ and a $^2\Sigma^+$ state, have an interesting physical explanation.[14] In terms of the vector model and old quantum theory, we have, say, an l vector which for small J values precesses around the electric axis giving $\Lambda=0$ ($^2\Sigma$ state) or $\Lambda=1$($^2\Pi$ state). The rotation of the molecule, however, causes a partial uncoupling of l. At the same time there is an uncoupling of S in the $^2\Pi$ state. The l-uncoupling produces an average component of l along the axis of rotation, i.e. essentially along K. In the limit of complete uncoupling, l is oriented with reference to R, now the quantum number of nuclear rotation, in such a way that $K-R=+l$ for the $^2\Sigma$ levels if for small J values the $^2\Pi$ is above the $^2\Sigma$, $K-R=0$ for the T_c levels of $^2\Pi$, and $K-R=-l$ for the T_d levels of $^2\Pi$ if the $^2\Pi$ is above the $^2\Sigma$. If the $^2\Sigma$ is above the $^2\Pi$, $K-R=-l$ goes with $^2\Sigma$, $K-R=+l$ with $^2\Pi^d$. For partial uncoupling, we may assume that l has a component, which we may call ρ, parallel to K, with values proportional to $\pm l$, 0, and $\mp l$ for $^2\Sigma$, $^2\Pi^c$, and $^2\Pi^d$.

The spin doubling $\Delta\nu_{12}$ in $^2\Sigma$ states can be explained, following Kemble and Van Vleck, as caused by the interaction of the electron spin with the component of the magnetic field of l corresponding to ρ[1,14], the linear variation of $\Delta\nu_{12}$ with $K+\frac{1}{2}$ corresponding to a proportionality of ρ approximately to K. The spin doubling in $^2\Pi$ states is ordinarily explained by the interaction of the spin with the component of the magnetic field of l corresponding to Λ. The variation of the spin doublet width $\Delta\nu_{12}$ with J caused by spin uncoupling is then given by the Hill and Van Vleck formula. But this neglects the possibility of l-uncoupling. When there is appreciable l-uncoupling, the ρ component of the magnetic field may become important and contribute to $\Delta\nu_{12}$. If from the total $\Delta\nu_{12}$ we deduct the $\Delta\nu_{12}$ calculated according to Hill and Van Vleck,[14a] the residuum should correspond to the interaction of the spin with ρ, and, from the considerations of the preceding paragraph, should for the $^2\Pi^c$ levels be approximately zero, but for the $^2\Pi^d$ levels should be approximately equal but opposite in sign to the doubling in the correlated $^2\Sigma$ state. [All this applies for the case that the $^2\Sigma$ state is $^2\Sigma^+$, but analogous statements can be made if it is $^2\Sigma^-$.] These conclusions are in agreement with the formal results given by Eqs. (20c), (20d), and (18), (19).

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[14] Cf. F. Hund, Zeits. f. Physik **52,** 606 (1929); W. W. Watson, Phys. Rev. **34,** 1010 (1929) and Ref. 19; R. S. Mulliken, Rev. Modern Physics **2,** (1930), pp. 99–100, Fig. 13, and especially Ref. 44a and Section (2) at top of p. 107; also corrections in **2,** 506–7 (1930). The part of $\Delta\nu_{12}(K)$ arising from the magnetic field of the ρ component of l is that corresponding to the coefficient γ in Eqs. (33)–(36) of the two references of Mulliken just cited.

[14a] If the l-uncoupling is very large, so that the component of l parallel to the electric axis becomes appreciably less than the original Λ, the Hill and Van Vleck part of $\Delta\nu_{12}$ should of course be somewhat less than that calculated by their formula. This, however, does not affect the qualitative relations to be expected.

One cannot expect to demonstrate the relations just discussed except in cases where simultaneously (1) A is fairly large so as to give easily measurable $\Delta\nu_{12}$'s; (2) the spin uncoupling is fairly complete at moderate J(A must not be *too* large); (3) the l-uncoupling is large at moderate J. This set of conditions is rarely fulfilled, but a good example of it is found in the CaH molecule (cf. Fig. 4, inset), which will be further discussed later in this paper.

A result, usually overlooked,[14] of the preceding considerations, is that $\Delta\nu_{12}(K)$ does not necessarily asymptotically approach zero with increasing K in $^2\Pi$ states. The above argument shows that this asymptotic approach to zero is usually to be expected in the T_c levels, but that in the T_d levels, $\Delta\nu_{12}(K)$ may go to a minimum and then increase again (ρ negative, $^2\Pi$ above $^2\Sigma^+$, if $A>0$) or may go through zero and increase again with opposite sign (ρ positive, $^2\Pi$ below $^2\Sigma^+$, if $A>0$). The latter behavior is observed in CaH (cf. Fig. 4).

Empirical Verification of the Theory, with Applications to Interpretation of Band Structures

It is of interest to compare the equations given above with experimental data, and to seek to determine and interpret the coefficients p, q, and γ. As Van Vleck has earlier shown, experimental data are in excellent agreement

Table I. Λ-*Type doubling in case b′* Π *states (all* $^1\Pi$, *except* $^3\Pi$ *in* He_2).

Molecule	Probable Elec. Configuration	Elec. Config. of Interacting State	B^*_v Values		$\nu_0(\Pi, \Sigma)$	$\nu(\Pi,\Sigma)$	q_0 calc'd for "pure precession"	q_0 obs'd
			Π^d	Σ				
H_2	$1s\sigma 2p\pi[C]$; $v=0$	$1s\sigma 2p\sigma[B]$	30.0	19.45	+9003	8130	+0.425	+0.7
	1		29.0			9060	0.348	0.6
	2		27.2			10100	0.289	0.6
BH	$\cdots 2s\sigma^2 2p\sigma 2p\pi$	$\cdots 2s\sigma^2 2p\sigma^2$	11.938	11.80	+23074	23070	+0.0246 (Eq. 7) +0.0492 (Eq. 7a)	+0.03
AlH	$\cdots 3s\sigma^2 3p\sigma 3p\pi$; $v=0$	$\cdots 3s\sigma^2 3p\sigma^2$	6.08	6.33	+23471	23430	+0.0060 (Eq. 7) +0.0120 (Eq. 7a)	+0.0057
	1		5.46			21960	0.00545 (Eq. 7) 0.0109 (Eq. 7a)	0.0050
He_2	$1s\sigma^2 2p\sigma 2p\pi$	$1s\sigma^2 2p\sigma 3p\sigma$	7.34	6.85	−6107	−6150	−0.035	−0.024
Li_2	$\cdots 2s\sigma 2p\pi$	$\cdots 2s\sigma 3p\sigma$	0.553	0.495	+6373	6250	+0.00017	+0.00020
Na_2	$\cdots 3s\sigma 3p\pi$	$\cdots 3s\sigma 4p\sigma$	0.1254	0.1085	+5295	5280	+0.0000118	+0.000013

Explanation and Notes. For each Π state given there seems to be one definite Σ state which stands to it in the relation of "pure precession," as is indicated by the fact that this assumption gives calculated values of q_0 in rather good agreement with the observed values. The observed q_0 values given (obtained in accordance with Eqs. 4 and 27), and the B^*_v values given, are for $v=0$ unless otherwise indicated. The calculated q_0 values are from Eq. (7) or (7a), using B_v of the Π state, and using for $\nu(\Pi,\Sigma)$ not the value $\nu_0(\Pi,\Sigma)$ corresponding to the transition between the levels $v=0$ of the Π and Σ states, but a somewhat different ν estimated by projecting vertically downward (or upward) from the $U(r)$ curve of the Π state to that of the Σ state (cf. text, p. 109). *In addition to the examples given, several nearly perfect cases of pure precession exist in the* $1s\sigma^2 2p\sigma nd(\sigma,\pi,\delta)$ *states of* He_2, others in H_2. The uncoupling in these cases is so great, however, that Van Vleck's equations do not hold well. A number of further examples of $\cdots np\pi$, $^1\Pi$ and $^3\Pi$ states in He_2 are also known which do obey Eq. (4).

The B^*_v values given are related to the true B_v values as follows: $B^*_v=B_v+(C+C_1)$ for $^1\Pi^c$ (T_c terms of $^1\Pi$), $B^*_v=B_v+(C+C_2)$ for $^1\Pi^d$ (cf. Eq. 3), while for $^1\Sigma$ states $B^*_v=B_v-C_3$, where C_3 represents the summation given in Eq. (8). Usually the B^*_v values are empirically more directly obtained for the Π^d than for the Π^c levels, hence in the table they are given for the former. The B^*_v values for Π^c can, however, be obtained simply by subtracting the observed q_0 value from B^*_v of Π^d. For pure precession with $l=1$, and a Σ^+ state, $C=0$, $C_2=0$, and $C_1=-C_3=q_0$. Hence for the T_c levels, $B^*_v=B_v$ is expected in this (usual) case.

The experimental data used were from the following sources: H_2, T. Hori, Zeits. f. Physik **44,** 845–6 (1927); B_v of the $^1\Sigma$ state is as calculated by H. Hyman, Phys. Rev. **36,** 187 (1930); BH, W. Lochte-Holtgreven and E. S. Van der Vleugel, Nature **127,** 236 (1931); R. F. Paton and G. M. Almy (private communication; cf. abstract No. 129, Washington Meeting American Phys. Soc., 1931); AlH, E. Bengttson and E. Hulthén, Zeits. f. Physik **52,** 275 (1928); E. Bengtsson and R. Rydberg, Zeits. f. Physik **59,** 546(1930); He_2, G. H. Dieke, S. Imanishi and T. Takamine, Zeits. f. Physik **57,** 305 (1929); W. E. Curtis, Proc. Roy. Soc. **A 118,** 157 (1928); W. E. Curtis and A. Harvey, Proc. Roy. Soc. **A 125,** 484 (1929); Li_2, K. Wurm, Zeits. f. Physik **58,** 562; **59,** 35 (1929); Na_2, F. W. Loomis and R. W. Wood, Phys. Rev. **32,** 223 (1928), and W. R. Fredrickson, Phys. Rev. **34,** 207 (1929).

TABLE II. Λ-*Type doubling in* $^2\Pi$ *states and spin doubling in* $^2\Sigma$ *states.*

Molecule	State	Probable Elec. Configuration	A	B_v or B^*_v	$Y=A/B_v$	$\nu_0(\Pi,\Sigma)$	$\nu(\Pi,\Sigma)$	Calc'd (pure precession)			Obs'd		
								p_0	γ_0	q_0	p_0	γ_0	q_0
BeH	$^2\Sigma^+$	$1s\sigma^2 2s\sigma^2 2p\sigma$		10.16		20032	20040		0.00399			0	
	$^2\Pi$	$1s\sigma^2 2s\sigma^2 2p\pi$	1.97	10.30	0.191		20030	0.00405		0.0212	—		0.0142
MgH	$^2\Sigma^+$	$\cdots 3s\sigma^2 3p\sigma$		5.70		19217	19310		0.0414			very small	
	$^2\Pi$	$\cdots 3s\sigma^2 3p\pi$	35	6.0	5.74		19070	0.0449		0.00780	0.04		0.002
	$^2\Pi$	$\cdots 3s\sigma^2 4p\pi$	4?	6.1	0.7?						—		0.021
CaH	$^2\Sigma^+$	$\cdots 4s\sigma^2 3d\sigma$		4.23		14432			(cf. text)			0.045	
	$^2\Pi$	$\cdots 4s\sigma^2 4p\pi$	79.6	4.29	18.5		−1320	−1.04		−0.056	−0.704		−0.067
	$^2\Sigma^+$	$\cdots 4s\sigma^2 4p\sigma$		4.40		−1322	−1320		−1.06			−0.945 or −0.543 (cf. Fig. 3)	
ZnH	$^2\Sigma^+$	$\cdots 4s\sigma^2 4p\sigma$		6.54		23429	23820		0.374			0.248	
	$^2\Pi$	$\cdots 4s\sigma^2 4p\pi$	341.5	7.31	46.7		23160	0.431		0.0092	0.277		0.004
	$^2\Sigma^+$	$\cdots 4s\sigma 4p\sigma^2$		3.4		−5811							
CdH	$^2\Sigma^+, v=0$	$\cdots 5s\sigma^2 5p\sigma$		5.32		22778	23000		0.926			0.59	
	1			5.04			23050		0.875			0.54	
	2			4.71			23500		0.802			0.48	
	3			4.32			25000		0.692			0.40	
	4			3.81			25900		0.589			0.30	
	$^2\Pi, v=0$	$\cdots 5s\sigma^2 5p\pi$	1001	5.99	167		22000	1.090		0.0065	0.62		0.0004
	1			5.75	174		22600	1.019		0.0058	0.44		0.0004
	$^2\Sigma^+, v=0$	$\cdots 5s\sigma 5p\sigma^2$		2.91		−5581						(Cf. Fig. 3)	
	1			2.79									
	4			2.59									
HgH	$^2\Sigma^+, v=0$	$\cdots 6s\sigma^2 6p\sigma$		5.39			28700		2.77			2.08	
	1			4.94			27500		2.65			1.78	
	2			4.35			29200		2.19			1.27	
	3			3.25			31400		1.52			0.75	
	4			1.45			31400		0.68			0.00	
	$^2\Pi_{1/2}, v=0$	$\cdots 6s\sigma^2 6p\pi$	3684	6.58	560	24933	23730	3.79		0.0068	3.26		—
	$^2\Pi_{1\frac{1}{2}}, v=0$					28617	27410						
	$^2\Pi_{1/2}, v=1$		3684	6.36	580		23900	3.64		0.0063	2.84		—
	$^2\Pi_{1\frac{1}{2}}, v=1$						27590						
	$^2\Sigma^+, v=0$	$\cdots 6s\sigma 6p\sigma^2$		4.09		−8943 from $^2\Pi_{1/2}$, $v=0$						0.95? (cf. Fig. 3)	

TABLE II. (*Cont.*)

Molecule	State	Probable Elec. Configuration	A	B_v or B^*_v	$Y=A/B_v$	$\nu_0(\Pi,\Sigma)$	$\nu(\Pi,\Sigma)$	Calc'd (pure precession)			Obs'd		
								p_0	γ_0	q_0	p_0	γ_0	q_0
CH	${}^2\Pi$	$\cdots 2p\sigma^2 2p\pi$	+28.4	14.207	+2.0		{−26270	+0.0614	(See text)	+0.0307}	+0.032		+0.037
							−31810	−0.0507		−0.0253}			
	${}^2\Delta$	$\cdots 2p\sigma 2p\pi^2$		14.60									0.000
	${}^2\Sigma^-$	$\cdots 2p\sigma 2p\pi^2$		12.62		−25715	−25180	(See text)	−0.0564	(See text)		−0.01(?)	
	${}^2\Sigma^+$	$\cdots 2p\sigma 2p\pi^2$		14.24		−31810	−31810		−0.0508			0	
SiH	${}^2\Pi$	$\cdots 3p\sigma^2 3p\pi$	+144	7.4	+19.5						0.049		0.0154
OH	${}^2\Pi$	$\cdots 2p\sigma^2 2p\pi^3$	−138	18.47	−7.45		−32710	+0.311		−0.0417	+0.231		−0.038
	${}^2\Sigma^+, v=0$	$\cdots 2p\sigma 2p\pi^4$		16.95		−32410	−32060		+0.292			+0.22	
	1			16.00			−30620		+0.289			+0.21	
HCl⁺	${}^2\Pi, v=0$	$\cdots 3p\sigma^2 3p\pi^3$	−637	9.80	−66.6		−29780	+0.839		−0.0126	+0.563		−0.0057
	$v=1$			9.46	−67.4		−28080	+0.859		−0.0128	+0.52		−0.0057
	${}^2\Sigma^+, v=0$	$\cdots 3p\sigma 3p\pi^4$		7.25		−28195	−23550		+0.893			+0.58	
	1			7.00			−20510		+0.956			+0.58	
	2			6.75			−17860		+1.02			+0.57	
N_2^+	${}^2\Sigma^+_g$	$\cdots 3p\sigma^2 2p\pi^4 3d\sigma$		1.922								|<0.005|(?)	
	${}^2\Sigma^-_u$	$\cdots 3p\sigma 2p\pi^4 3d\sigma^2$		2.074								+0.016 (?)	
BO	${}^2\Sigma^+$	$\cdots 3p\sigma^2 2p\pi^4 3d\sigma$		1.779		+23584						<0.005	
	${}^2\Pi$	$\cdots 3p\sigma^2 2p\pi^3 3d\sigma^2$	−123	1.408	−87						+0.022		−0.00019
	${}^2\Sigma^+$	$\ldots 3p\sigma 2p\pi^4 3d\sigma^2$		1.512		−19281						?	
NO	${}^2\Pi, v=2$	$\cdots 2p\pi^4 3d\pi$	+124	1.648	+75	−44132					+0.015		+0.00035
	${}^2\Sigma^+$	$\cdots 2p\pi^4 3s\sigma$		1.971								|<0.02|	
	${}^2\Pi$	$\cdots 2p\pi^3 3d\pi^2$	+32	1.118	+28.6	+1308					0.00 (probably)		
O_2^+	${}^2\Pi_g, v=8$	$\cdots 2p\pi^4 3d\pi$	+195	1.530	+128						+0.020		+
	${}^2\Pi_u, v=0$	$\cdots 2p\pi^3 3d\pi^2$	+8	1.043							very small		very small

Explanation and Notes. The general remarks under Table I in the main also apply here. The observed values of p_0, q_0, and γ_0 are obtained in accordance with Eqs. (14), (18), (26), (27), or also (14a), (14b) for pronounced case *a*. The calculated values are from Eqs. (12), (19). In calculating p_0, B_v of the corresponding Π state is used, in calculating γ, B_v of the corresponding Σ state; $\nu(\Pi,\Sigma)$ is obtained in either case by vertical projections from the state whose coefficient is to be calculated to the $U(r)$ curve of the other state involved in the "pure precession" (cf. text). The electron configurations given are largely from R. S. Mulliken, Phys. Rev. **33,** 737 (1929).

The B^*_v or B_v values given in the table are always B^*_v values in the case of ${}^2\Sigma$ states. Here $B^*_v=B_v-C_3$, where C_3 is a quantity given by Eq. (16). For pure precession with $l=1$, C_3 should be the same as q_0 of the ${}^2\Pi$ state, (or $-q_0$ in the case of a ${}^2\Sigma^-$ state). For case *b* ${}^2\Pi$ states, the table gives B^*_v values of ${}^2\Pi^d$, just as Table I gives B^*_v values of ${}^1\Pi^d$ (cf. Notes to Table I); the case *b* states in Table II are those of BeH, MgH (upper ${}^2\Pi$), CH and OH. For case *a* ${}^2\Pi$ states, Table II gives approximately the true B_v values, obtained by averaging the B^* values B^*_1 and B^*_2 corresponding to the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{1\frac{1}{2}}$ states.

The experimental data used were from R. S. Mulliken, Phys. Rev. **32,** 388 (1928); **33,** 507 (1929) and sources there cited, and from the following original or secondary sources:

1. BeH, W. W. Watson and A. E. Parker, Phys. Rev. **37,** 167 (1931).
2. MgH, R. W. B. Pearse, Proc. Roy. Soc. **A 122,** 442 (1929).
3. CaH, E. Hulthén, Phys. Rev. **29,** 97 (1927); R. S. Mulliken, Phys. Rev. **30,** 138 (1927); W. W. Watson and W. Bender, Phys. Rev. **35,** 1513 (1930).
4. ZnH, upper ${}^2\Sigma$ state, E. Bengtsson and E. Hulthén, Faraday Soc. Proc. **25,** 751 (1929).
5. CdH, E. Svensson, Zeits. f. Physik **59,** 333 (1930).
6. HgH, E. Hulthén, Diss. Lund, 1923; Zeits. f. Physik **32,** 32 (1925); **50,** 319 (1928).
7. CH, T. Hori, Zeits. f. Physik **59,** 91 (1929); and references cited in R. S. Mulliken, Phys. Rev. **30,** 785 (1927).
8. SiH, R. S. Mulliken, Phys. Rev. **37,** 733 (1931).
9. OH, G. H. Dieke, Proc. Acad. Sci. Amsterdam **28,** 174 (1925); G. M. Almy, Phys. Rev. **35,** 1495 (1930).
10. HCl⁺, M. Kulp, Zeits. f. Physik **67,** 7 (1931).
11. N_2^+, M. Fassbender, Zeits. f. Physik **30,** 73 (1924); R. S. Mulliken, Phys. Rev. **30,** 138 (1927).
12. BO, A. Elliott: Diss. Utrecht, 1930; W. Scheib, Zeits. f. Physik **60,** 73 (1930).
13. NO, M. Guillery, Zeits. f. Physik **42,** 127 (1927).
14. O_2^+, D. S. Stevens, Abstract No. 134, Washington Meeting Am. Phys. Soc. 1931. The signs (+) of p_0 and q_0 for the lower ${}^2\Pi$ are based on the very probable assumption that this is ${}^2\Pi_g$ as given in the table and on the safe assumption that the observed rotational levels have ψ functions which are symmetrical in the nuclei.

with the relations predicted by the theory for $^2\Sigma$ and $^2\Pi$ states in the limiting cases a and b, and for $^1\Pi$ states. Our purposes here include (1) a study of the applicability of Van Vleck's general equation (our Eq. 9 or 14) to $^2\Pi$ states in the intermediate cases between a and b, and (2) determination of the magnitudes and signs of the coefficients p, q, and γ for a number of molecular states. In a following section we shall examine more carefully than has been done before whether the values of p, q, and γ are in agreement with what would be expected theoretically from our knowledge of the electron levels of the molecules in question; and conversely, we shall use the values of p, q, and γ as a means of getting information about electron configurations or other properties of electron levels.

Tables I and II give the sign and magnitude of q of Eq. (4) for some $^1\Pi$ states, of p and q for several $^2\Pi$ states (cf. Eqs. 10, 14) and of γ for a number of $^2\Sigma$ states (cf. Eq. 18). [Really, values of p_0, q_0, and γ_0 are given in the tables. The relation of these to p, q, and γ is explained in the next section.] The sources of data are given in the notes to the tables. The values of p and q given in Tables I and II, where they differ from those given or implied in an earlier paper[15] dealing briefly with similar subject matter, are to be taken as superseding the latter. In preparing Tables I and II, much care has been taken to obtain correct signs and magnitudes of p, q, and γ, but it is not unlikely that some errors are present.

Modification of theoretical formulas to take care of variation of mean moment of inertia with J and with v. In the course of the work we found that, while the forms of Van Vleck's equations are such as to fit the experimental data nearly always extremely well for low and moderate J values, rather large deviations seem to occur when data for high J values are used. Now in all Van Vleck's equations there appears as a factor the matrix element BL_y or $|BL_y|^2$, in which $B=h/8c\pi^2I$, where $I(=\mu r^2)$ represents the moment of inertia. Approximately, it is seen to be possible to take out B as a factor and set it equal to B_v(cf. e.g. Eq. 5a). In the case of a non-vibrating molecule, we have $B=B_e=h/8c\pi^2\mu r_e^2=h/8c\pi^2 I_e$ in the limit of zero angular velocity of rotation. But if the molecule rotates, it stretches slightly, or if the rotation is very fast, it stretches considerably, i.e., r becomes greater than r_e. From the way in which Van Vleck's BL_y and B are defined, it is clear that allowance should be made, in applying his equations, for the effect of such stretching on B and BL_y.

For a non-vibrating diatomic molecule with $\Lambda=0$ and $S=0$ the kinetic energy of rotation is given[16] by

$$P_\phi^2/2\mu r^2 = [P_\phi^2/2\mu r_e^2](r_e/r)^2 = hcB_eK(K+1)[1/(1+\xi)^2], \qquad (21)$$

where P_ϕ is the angular momentum, equal to $K(K+1)h/2\pi$ according to quantum theory, while $\xi=(r-r_e)/r_e$, a quantity which is a measure of the stretching by rotation.

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[15] R. S. Mulliken, Phys. Rev. **33**, 507 (1929).

[16] Cf. e.g. R. S. Mulliken, Ref. 14, p. 65.

If ξ is not too large, we may assume that the stretching takes place against a force whose potential energy is given by

$$U(r) = a^*\xi^2/2, \text{with } a^* = 4\pi^2 c^2 \omega_e^2 \mu r_e^2 = hc\omega_e^2/2B_e, \tag{22a}$$

$c\omega_e$ being the frequency of infinitesimal classical vibrations about $r=r_e$. In this case, it is easily found [16] that ξ is given by

$$\xi = u^2 K(K+1), \text{where} \tag{22b}$$

$$u^2 = 4B_e^2/\omega_e^2 = -D_e/B_e, \tag{22c}$$

D_e being a coefficient determinable from an analysis of the rotational energy levels. Ordinarily $u^2 \ll 1$. Eqs. (22a), (22b) show how r increases with K.

Assuming Eq. (22a), one can write, according to Eqs. (21), (22b),

$$\begin{aligned} B_{\text{K}} &\equiv h/8\pi^2 c\mu r^2 = B_e/(1+\xi)^2 \\ &= B_e/[1 + u^2 K(K+1)] \sim B_e[1 - 2u^2 K(K+1) + \cdots]. \end{aligned} \tag{23}$$

On adding to the kinetic energy of rotation as given by Eqs. (21) and (23), the potential energy $U(r)$ given by Eq. (22a), and dividing by hc, one gets the ordinary rotational spectroscopic term $F(K)$. The result can be reduced[16] to:

$$F(K) = B_e K(K+1) + D_e K^2(K+1)^2 + \cdots.$$

For a vibrating molecule, one gets essentially the same results, in particular

$$B_{v,\text{K}} = h/8\pi^2 c\mu \overline{r_v^2} \tag{24a}$$

$$\sim B_v/[1 + u^2 K(K+1)] \tag{24b}$$

$$\sim B_v[1 - 2u^2 K(K+1) + \cdots] \tag{24c}$$

$$F(K) = B_v K(K+1) + D_v K^2(K+1)^2 + \cdots. \tag{25}$$

Eq. (24a) defines a kind of mean r for any vibrational state[16a]. Since in practise B_v usually decreases with increasing v, this mean r increases with v.

For molecules with $\Lambda > 0$ or $S > 0$ the rotational term $F(K)$ becomes more complicated than the form given by Eq. (25), but the variation of B_v with the rotational quantum number is always given with sufficient accuracy by Eq. (24b) or (24c). Often J rather than K, or something slightly different from both, is needed in Eqs. (24), but this makes very little difference in the result.

Proper allowance can now evidently be made, in Van Vleck's equations, for rotational stretching by using $B_{v,\text{K}}$ instead of B_v. Since $B_{v,\text{K}}$ varies with K, the coefficients p, q, and γ in Van Vleck's equations should likewise vary with K. The coefficients p and γ, which according to the theory involve BL_y, should vary with K in the same way that $B_{v,\text{K}}$ does, while q, which according to the theory involves $|BL_y|^2$, should vary in the same way that $(B_{v,\text{K}})^2$ does. In other words, we expect, for any given value of v,

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[16a] Cf. R. T. Birge, Nat. Research Council Report on Molecular Spectra, p. 112, Eq. (48).

$$p = p_0/[1 + u^2K(K+1)] \sim p_0[1 - 2u^2K(K+1) + \cdots], \qquad (26a)$$

$$\gamma = \gamma_0/[1 + u^2K(K+1)] \sim \gamma_0[1 - 2u^2K(K+1) + \cdots], \qquad (26b)$$

$$q = q_0/[1 + u^2K(K+1)]^2 \sim q_0[1 - 4u^2K(K+1) + \cdots]. \qquad (27a)$$

Likewise for varying v and fixed K we may reasonably expect

$$p_0 \text{ and } \gamma_0 \text{ proportional to } B_v, \qquad (26c)$$

$$q_0 \text{ proportional to } B_v^2 \qquad (27b)$$

Since $u \ll 1$, it is of course only when K or J is large that p, q, and γ differ appreciably from p_0, q_0, and γ_0. *The coefficients p_0, q_0, and γ_0 given in Tables I and II have been mainly determined from data for low and moderate J values, where the effect of the stretching of the molecule on p, q, and γ is still negligible.* Eqs. (26) and (27) have been used mainly only to explain the variation of these coefficients with J which is observed at high J values. In some cases, however, the values of the coefficients have been adjusted slightly in order to give better agreement at high J values.

In applying Eqs. (26) and (27), either of the two forms ($4B_e^2/\omega_e^2$ or $-D_e/B_e$) of the quantity u^2(cf. Eq. 22c) may be used. The choice depends on the relative accuracy, or on the existence, of available data for D_e and ω_e. In the following work, sometimes the one, sometimes the other choice has been found best.

A particularly good example of the effect of the variation of q with K is seen in the case of BeH (Fig. 2). Here we have a case b $^2\Pi$ state to which Eq. (4) applies. According to Eq. (4) , if q is a constant, $\Delta\nu_{dc}(K)$ should be proportional to $K(K+1)$. Actually, $\Delta\nu_{dc}$ goes to a maximum as K increases to large values, then shows a tendency to decrease. But this behavior can probably be completely accounted for (cf. Fig. 2, caption) by the variation of q with K which is predicted by the foregoing considerations. In other molecules, similar behavior of $\Delta\nu_{dc}$ can always be partly accounted for in the same way, although usually some deviations from the simple Van Vleck formulas still remain to be accounted for in other ways. These will be discussed later.

The proportionality of p, γ, and q to B_v or B_v^2 which is predicted by Eqs. (26c) and (27b) is found to be at least qualitatively fulfilled in all cases (cf. Tables I and II) except those of certain states where there are strong perturbations (upper $^2\Sigma$ states of CdH, HgH in Fig. 3) and where one would not expect the equations to hold.

Determination of coefficients p_0, q_0, and γ_0. It will be well at this point to explain how one obtains the doublet separations $\Delta\nu_{dc}$ and $\Delta\nu_{12}$ used as a basis for the determination of p_0, q_0, and γ_0 of Tables I and II. For the way in which the $\Delta\nu_{12}$'s are determined (and the uncertainties involved in some cases), the reader may be referred to some earlier papers.[17] The problem of determining the $\Delta\nu_{dc}$'s resolves itself into two parts, namely determination of the *signs* and of the *magnitudes* of these quantities.

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[17] Cf. R. S. Mulliken, Phys. Rev. **30**, 138, 1927 ($^2\Sigma$, $^2\Sigma$ bands); Phys. Rev. **30**, 785, 1927 and **32**, 388, 1928 ($^2\Pi$,$^2\Sigma$ and $^2\Sigma$, $^2\Pi$ bands), also the figures in Ref. 4.

The sign of $\Delta\nu_{dc}$ for the rotational levels of any Π state can always be determined if combinations of the Π state with a Σ state are known, and if it is known whether the Σ state is a Σ^+ or a Σ^- state. Since the + or − character of every rotational level is then known for the Σ state (cf. Ref. 4, Fig. 17), and since the selection rule $+ \longleftrightarrow -$ is obeyed (cf. Ref. 4, p. 96) in all band lines (with very rare exceptions resulting from the influence of electric fields), one can determine the + or − character of each rotational level of the Π state. This makes it possible to assign the theoretically defined labels *c* and *d* to each level, and so, the positions of the levels having been determined from analysis of the band structure, to determine the sign of $\Delta\nu_{dc}$. Reference to Figs. 17, 25, 28 of Ref. 4 will help to make the method clear.

The above method obviously depends on knowing whether the Σ state used in the process is a Σ^+ or Σ^- state. This cannot be determined empirically, but can nearly always be decided with practical certainty on theoretical grounds. Nearly always in dealing with $^1\Sigma$ and $^2\Sigma$ states, one encounters Σ^+ states. Σ^- states cannot occur except in the case of molecules having two (or an even number of) π electrons which are not in closed shells (or in similar cases, never yet found, involving δ, ϕ electrons). Thus a knowledge of its electron configuration is usually sufficient to determine whether a Σ state is Σ^-.

In the case of every state listed in Tables I and II, with one exception (SiH, see below), Π, Σ bands have been analyzed and the electron configuration of the Σ state is known with practical certainty, at least to the extent that is necessary to establish whether it is Σ^+ or Σ^-. In only *one* case, that of CH, is a Σ^- state involved; here the $^2\Pi$ combines with a $^2\Sigma^-$ and also with a $^2\Sigma^+$ state[18] both of which are derived from the same electron configuration . . . $2p\sigma 2p\pi^2$; supplementary considerations in regard to dissociation products here make it probable that the lower of the two $^2\Sigma$ states is $^2\Sigma^-$ and the upper $^2\Sigma^+$, and thus make it possible to fix the sign of $\Delta\nu_{dc}$ in the $^2\Pi$ state. The $^2\Pi$ state of SiH is known only from $^2\Delta$, $^2\Pi$ bands.[2] Such bands are always incapable of fixing the sign of $\Delta\nu_{dc}$. The probable close analogy of SiH to CH makes it probable, however, even with due regard for the possibilities involved in Eqs. (5), that *p* and *q* have the same sign in the $^2\Pi$ of SiH as in that of CH; this then serves to fix the sign of $\Delta\nu_{dc}$.

In determining the *magnitude* of $\Delta\nu_{dc}$, the procedure is usually simplest in the case of $^2\Delta,{}^2\Pi$ and $^2\Pi,{}^2\Delta$ bands. Here the doublet separations are usually negligible in the $^2\Delta$ states (this can always be checked, if doubtful, by a study of combination relations), and one gets $\Delta\nu_{dc}$ directly:

$$\Delta\nu_{idc} = R_{icid}(J) - R_{idic}(J) = Q_{id}(J) - Q_{ic}(J) = P_{icid}(J) - P_{idic}(J),$$

where $i = 1$ or 2,—cf. Fig. 26 of Ref. 4.

In determining $\Delta\nu_{dc}$ from Π, Σ or Σ, Π bands (cf. Figs. 17, 25, 28 of Ref. 4, also Ref. 17), one gets for instance

$$[R(J) - Q(J)] - [Q(J+1) - P(J+1)] = \Delta\nu_{dc}(J) + \Delta\nu_{dc}(J+1) \quad (28)$$

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[18] Cf. T. Hori, Zeits. f. Physik **59**, 918, 1929.

in the case of a $^1\Pi,^1\Sigma^+$ or $^2\Pi_{\frac{1}{2}},^2\Sigma^+$ or $^2\Pi_{1\frac{1}{2}},^2\Sigma^+$ transition. One may write

$$\Delta\nu_{dc}(J) + \Delta\nu_{dc}(J+1) \sim 2\Delta\nu_{dc}(J+\tfrac{1}{2}), \qquad (29)$$

i.e. one gets in this way not the real doublet separation $\Delta\nu_{dc}(J)$ for actual values of J, but instead the separations $\Delta\nu_{dc}(J+\frac{1}{2})$ for a set of fictitious J values half way between the members of the set of real J's. These quantities are, however, just as useful in determining p and q as the $\Delta\nu_{dc}(J)$'s would be.

$^2\Pi$ *states intermediate between cases a and b.* Before discussing the interpretation of the values of p_0, q_0, and γ_0 given in Tables I and II, we shall consider in some detail the applicability of Eq. (14) to several examples of $^2\Pi$ states intermediate between cases a and b, and the way in which the coefficients p_0 and q_0 were determined from experimental data. The examples chosen are the $^2\Pi$ states of ClH^+, OH, CH, CaH, SiH, ZnH, and HgH. A and B_v, hence Y of Eq. (14), are already known for these states from previous work. The empirical data on $\Delta\nu_{dc}(J)$ are obtained from $^2\Pi$, $^2\Sigma$ or $^2\Sigma$, $^2\Pi$ bands except in the case of SiH, where the $^2\Delta$, $^2\Pi$ bands are used.

Given a set of $\Delta\nu_{dc}$ data for each of the two sets of levels T_1 and T_2 or of the two substates $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ of a $^2\Pi$ state, one can often determine p_0 and q_0 independently for each set or substate. The values so determined should according to the theory be the same, at least very nearly, for the two sets. One can also use the data on both substates simultaneously so as to determine a p_0 and q_0 which apply to both.

Using the latter method, it will be seen that Eq. (14) predicts the following relation:

$$\Delta\nu_{2dc}(J) - \Delta\nu_{1dc}(J) = (p+2q)(J+\tfrac{1}{2}) + \cdots. \qquad (30)$$

Here $\Delta\nu_{2dc}$ refers to the T_2 levels, $\Delta\nu_{1dc}$ to the T_1 levels. On examining the data for the examples mentioned above, it was found that $\Delta\nu_{2dc}-\Delta\nu_{1dc}$ is accurately proportional to $(J+\frac{1}{2})$ up to moderate J values, but that considerable deviations from this proportionality set in for high J values. Thus for small and moderate J values the quantity p_0+2q_0 could be accurately determined from the data. The behavior of $\Delta\nu_{2dc}-\Delta\nu_{1dc}$ at high J values was always at least partly accounted for by means of Eqs. (26) and (27).

Next, by taking $\Delta\nu_{2dc}(J)+\Delta\nu_{1dc}(J)$, a more complicated expression than Eq. (30) is obtained, which depends largely on q and to a lesser extent (except for small J) on $(p+2q)$. By correcting for the terms involving $(p+2q)$, a set of empirical quantities proportional to $q(J-\frac{1}{2})(J+\frac{1}{2})$ $(J+3/2)$ is obtained. These give q, and the value of p then follows.

Values of p_0 and q_0 determined as just outlined are given in Tables I and II, while in Figs. 1 and 2 are shown theoretical curves for $\Delta\nu_{dc}(J)$ corresponding to Eqs. (14), (26), (27) for several of the molecular states whose p_0 and q_0 values are given in Table II. The empirical values of $\Delta\nu_{dc}(J)$ or $\Delta\nu_{dc}$ $(J+\frac{1}{2})$ are shown by small circles. It will be seen that the agreement is excellent, except in some cases for high J values. The disagreements at high J values would be worse if the variation of p and q with J had not been taken into account (cf., e.g., Fig. 2). Possible explanations of the remaining dis-

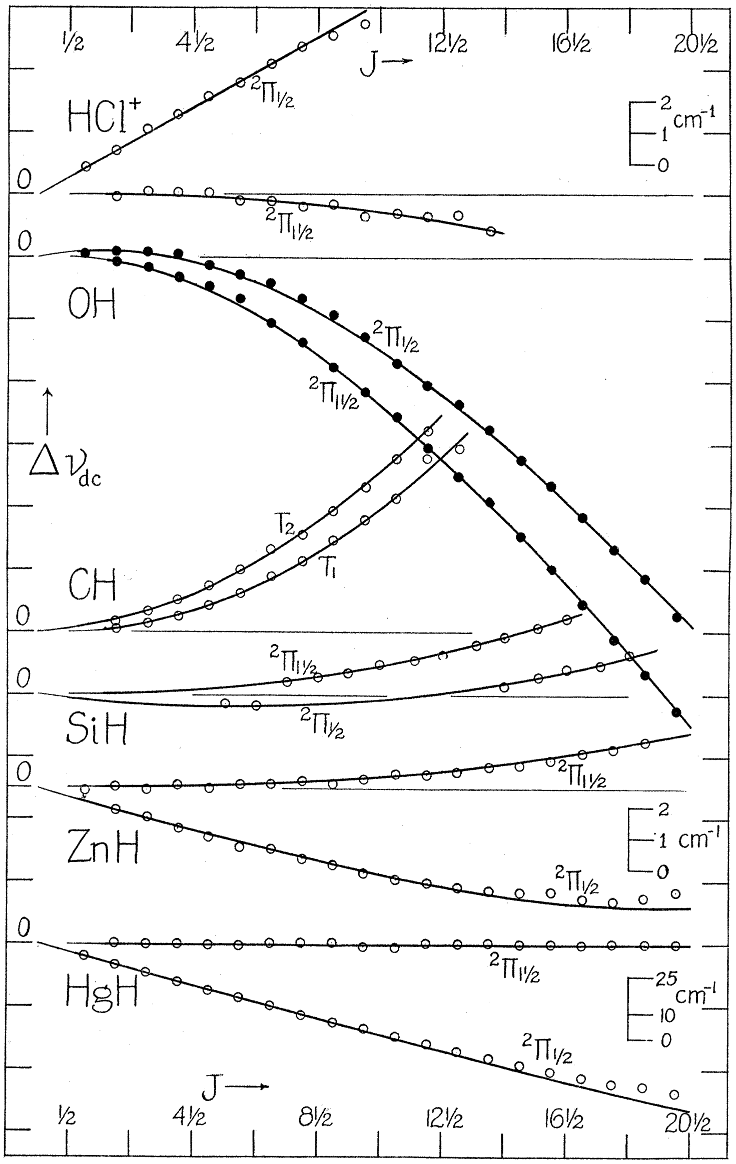

Fig. 1. Comparison of experimental data, indicated by circles, with theoretical curves drawn according to Eq. (14) for $\Delta\nu_{dc}(J)$ for $^2\Pi$ states of several hydride molecules having a variety of values of the parameter $Y=A/B$. The scale used is the same for all the molecules except HgH. Two further examples are shown in Fig. 2. The coefficients p_0, q_0 used in drawing the theoretical curves were chosen so as to fit the experimental data as well as possible. They are the "observed" values given in Table II. The slight variation in p and q for high J values (cf. Eqs. 26, 27) has been taken into account in drawing the theoretical curves for HgH, ZnH, and OH; the quantity $u^2=4B_e^2/\omega_e^2$ in Eqs. (26), (27) has been calculated using experimental ω values, or in the case of ZnH a value estimated from the empirical relation $\omega_e/B_e \sim$constant, using for the constant the value which is found in CuH.

crepancies will be taken up later. Empirical values of γ_0 are given in Table II, while Fig. 3 gives observational data for $\Delta\nu_{12}(K)$ for several examples of $^2\Sigma$ states.

Applications of theory to interpretation of band structure (SiH, CaH). The quantitative agreement of the data for SiH with Eq. (14) confirms the conclusions, reached in a previous paper[2] on the basis of a qualitative use of the same theory, as to the interpretation of the $^2\Delta,^2\Pi$ bands of SiH. Eq. (14) has also been used here to clear up an uncertainty as to the numbering of the lines of the Q_2 branch in the $^2\Pi$, $^2\Sigma$ bands of CaH. The numbering of the Q_1 lines in these bands was recently revised by Watson and Bender[19] on the basis of combination relations involving a previously undiscovered $^OP_{12}$ branch. This made it possible for them to determine also the quantities $\Delta\nu_{1dc}(J+\frac{1}{2})$ corresponding to the $^2\Pi_{\frac{1}{2}}$ sub-state. From these data we determined p_0 and q_0 of Eq. (14), and then used them to calculate the quantities $\Delta\nu_{2dc}$ applicable to the $^2\Pi_{1\frac{1}{2}}$ state. Knowing these and the frequencies of the

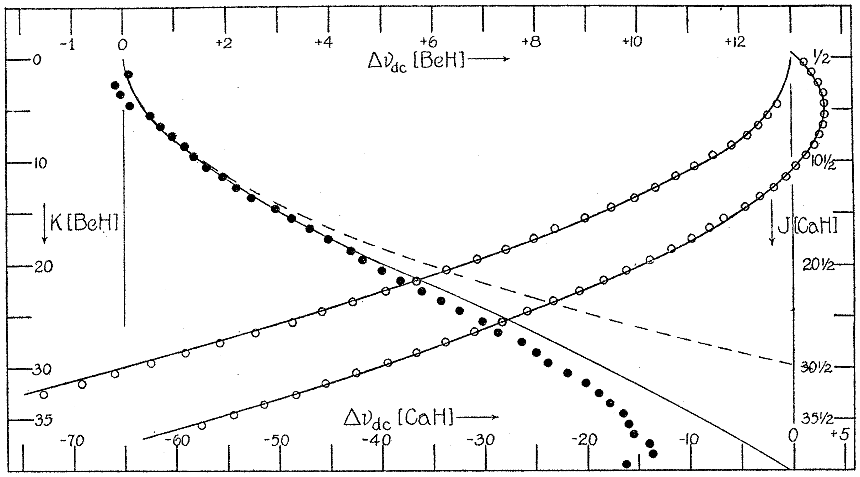

Fig. 2. Comparison of experimental data with theoretical curves for $\Delta\nu_{dc}$ for $^2\Pi$ states of BeH and CaH. Eqs. (14), (26), and (27) were used for CaH; the u value needed in Eqs. (26), (27) was calculated using $\omega=1300$, estimated (by means of the relation $\omega_e/B_e\sim$ constant) from the observed ω_e value[30] of the normal $^2\Sigma$ state. Eq. (4) and the exact form of Eq. (27) were used for BeH, which is case b and acts practically like a $^1\Pi$ state. The importance of using Eq. (27) for q instead of assuming a constant q in Eq. (4) is shown here. The dashed curve represents Eq. (4) drawn for $q=q_0$, while the full curve assumes a varying q in accordance with Eq. (27). The remaining discrepancy between the full curve and the experimental points can be attributed to the failure of the simple relation $U(r)=a^*\xi^2/2$ (cf. Eq. 22a) and consequently of Eq. (22b) at high K values. As is indicated by the course of the T values[26] themselves at the highest observed K values, the molecule stretches considerably more rapidly than in Eqs. (22a), (22b). Hence (cf. Eq. 23) $B_{v,K}$ and so q should, as observed, diminish more rapidly at the highest K values than Eq. (27) demands. In obtaining u in Eq. (27), the relation $u^2=-D_e/B_e$ has been used for BeH, with experimental values[26] of D_e and B_e. (In other cases shown in Figs. 1–3, the same effects as in BeH exist at high J values, but are not nearly so large.)

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[19] W. W. Watson and W. Bender, Phys. Rev. 35, 1513 (1930).

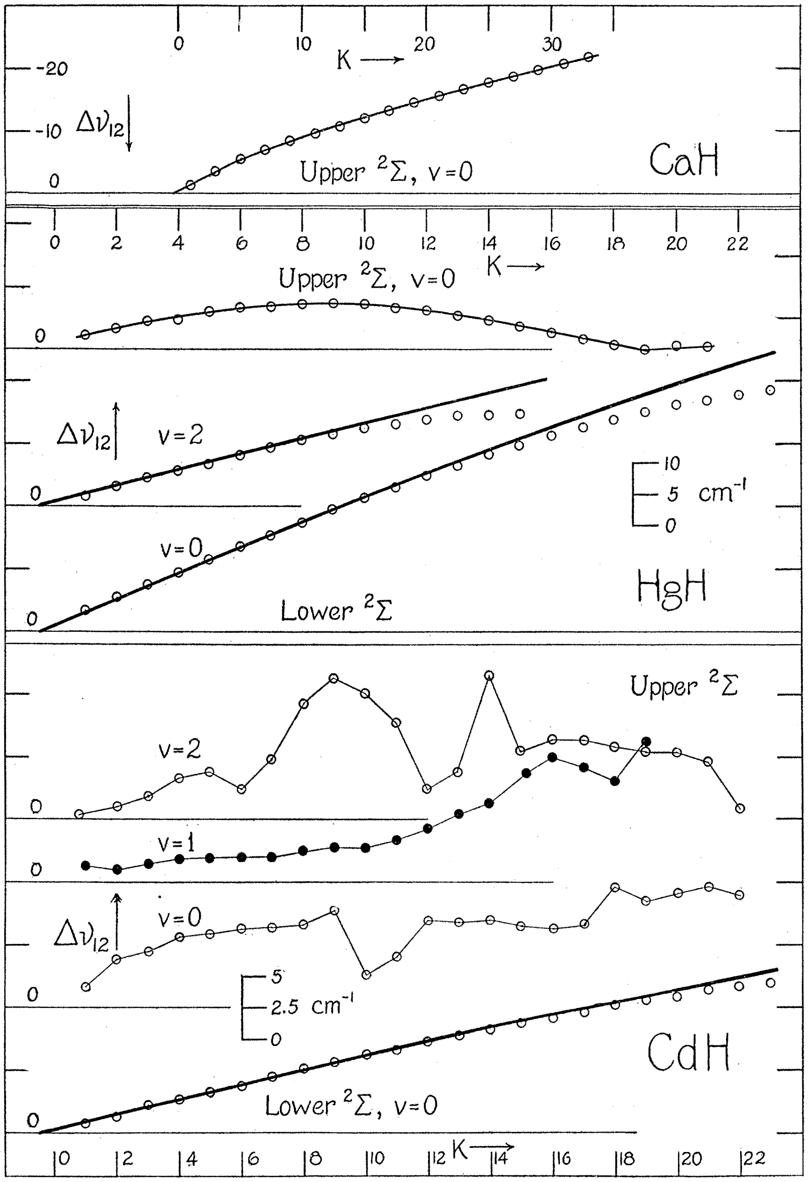

Fig. 3. Spin doublet separations $\Delta\nu_{12}(K)$ in $^2\Sigma$ states (cf. Eqs. 2, 18). The circles represent experimental values. The *heavy* curves (only for CdH, lower $^2\Sigma$, $v=0$ and for HgH, lower $^2\Sigma$, $v=0$ and 2) are theoretical curves corresponding to Eq. (18), (26). The coefficient γ_0 of these theoretical equations has been chosen in each case to give a best fit to the experimental data, while the quantity $u^2=4B_e^2/\omega_e^2$ needed in the second equation has been calculated using the experimental B_v values (Table II) and ω values ($\omega_{\frac{1}{2}}=1374$ for CdH, $\omega_0=1308$ for HgH). The considerable deviations of the experimental points from the calculated curves for high K values in HgH are tentatively attributed to changes in the electronic wave functions, hence in γ_0, with increasing K.

band-lines $P_2(J)$ and $R_2(J)$, it was possible to predict the positions of the band-lines $Q_2(J)$ with sufficient accuracy to determine the correct numbering of these lines.[20] From the P_2, Q_2, and R_2 branches, accurate values of $\Delta\nu_{2dc}$ were now obtained, and from the data on $\Delta\nu_{1dc}$ and $\Delta\nu_{2dc}$ improved p_0 and q_0 values were determined in the usual way.

As a check on the numbering of the Q_2 lines, the positions of the hitherto unassigned lines of the weak branch ${}^SR_{21}$ have been calculated on the basis of Eqs. (31) and (32).[21]

$$
\begin{aligned}
{}^SR_{21}(J) &= R_2(J) - \Delta\nu_{2dc}(J+1) + T_2''(J) - T_1''(J) \qquad (31)\\
&= Q_2(J+1) + T_2''(J-1) - T_1''(J-1). \qquad (32)
\end{aligned}
$$

The ${}^SR_{21}$ lines were calculated from Eq. (32), except for $J=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, where Eq. (31) had to be used owing to the absence of data on $Q_2(J)$. In Eq. (31), *calculated* values of the small quantities $\Delta\nu_{dc}(J+1)$ were used. For R_2 and Q_2 in Eqs. (31) and (32), empirical ν data were used directly, while the other quantities in these equations were obtained by suitable additions and subtractions of measured ν's.

Measurements on a second-order grating plate of the CaH bands (taken by Dr. P. S. Delaup in this laboratory in connection with his work on the Zeeman effect of these bands) disclosed a set of lines having appropriate intensity relations[22] and agreeing excellently in position with the values calculated for the ${}^SR_{21}$ branch (cf. Table III).

TABLE III. ${}^SR_{21}$ *Lines in* (0,0) *Band of* ${}^2\Pi,{}^2\Sigma^+$ *System of CaH.*

J	Calc'd ν	Obs'd ν	Int.	J	Calc'd ν	Obs'd ν	Int.
$\frac{1}{2}$	14,479.08	14,479.32	5	$6\frac{1}{2}$	14,573.43	14,573.46	2 (dif)
$1\frac{1}{2}$	493.33	493.42	2	$7\frac{1}{2}$	590.57	Masked by Q_1 $(39\frac{1}{2})$	
$2\frac{1}{2}$	508.29	Masked by $R_1(9\frac{1}{2})$		$8\frac{1}{2}$	608.59	608.55	1−
$3\frac{1}{2}$	523.75	523.87	1	$9\frac{1}{2}$	626.81	626.62	1−
$4\frac{1}{2}$	539.89	Masked by $R_1(12\frac{1}{2})$		$10\frac{1}{2}$	645.02	644.89	1−
$5\frac{1}{2}$	556.53	Masked by atomic line					

INTERPRETATION OF RESULTS IN RELATION TO ELECTRON CONFIGURATIONS

The values of p_0, q_0 and γ_0 given in Tables I and II have a significant bearing on the question of the forms of the electron orbits or of the wave functions for the molecules concerned. That the values of p_0, q_0, and γ_0 depend on these can be seen from Van Vleck's theoretical equations for them (cf. Eqs. 4, 5, 5a; 10, 10a, 10b; 17). In the simple case that a Σ and a Π state are to each other in the relation of "pure precession" (cf. discussion in two paragraphs preceding Eqs. 6 and 7), simple theoretical expressions can be given for p_0, q_0, and γ_0 (cf. Eqs. 6, 7, 7a, 12, 19).

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[20] As a result of the revised numbering of the Q_2 branches, the positions of the Q_2 (and ${}^QP_{21}$) lines shown in Fig. 30a of Ref. 4 should be revised, and in such a way (cf. Fig. 4 of the present paper) that the Q_1 and Q_2 branches *do not cross.*

[21] The correctness of these equations can be seen from Fig. 28 of Ref. 4.

[22] Cf. Ref. 4, pp. 140–141; also cf. data on the ${}^SR_{21}$ branch in the ${}^2\Sigma^+,{}^2\Pi$ bands of OH (R. S. Mulliken, Phys. Rev. **32**, 410, 1928).

Van Vleck pointed out in his paper[1] that the observed values of p, q and γ commonly are of an order of magnitude corresponding well to the case of pure precession. We now find that something like pure precession seems to be almost quantitatively fulfilled in most of the molecular states studied here. This rather surprising result appears to carry with it the important conclusion that in these molecules the electrons commonly have well-defined quantum numbers n and l having the same significance as in atoms. In some cases, in particular the hydrides, these quantum numbers n and l are those corresponding to the atom which would be obtained if the two nuclei could be united. In other cases, the n and l which are significant are found to be those which would exist if the two atoms were completely separated. The various relations which exist in different cases can best be brought out by a discussion of examples.

Calculation of p_0, q_0, γ_0 *for pure precession.* First, however, something needs to be said in regard to the method of obtaining the *calculated* values of p_0, q_0, and γ_0 in Tables I and II. The first step, in the case of a Π state, is to see whether there is a neighboring Σ state such that, using Eqs. (7), (7a), (12) with $\nu_0(\Pi, \Sigma)$, p_0 and q_0 come out roughly in agreement with the observed values. [By $\nu_0(\Pi,\Sigma)$ is mean the difference in E/hc between the level $v=0$ of the Π state and that of the Σ state.] In nearly all cases it turns out that just one such state is known, and that the agreement is good. The calculated values of p_0 and q_0 are then revised by replacing $\nu_0(\Pi, \Sigma)$ by a quantity $\nu(\Pi, \Sigma)$ obtained by projecting vertically downward (or upward, if the Σ level is above the Π) from the level $v=0$ of the Π state (or from the level $v=v$, if one wishes to calculate p_0 and q_0 for $v>0$) to the $U(r)$ curve of the Σ state. [In projecting "from the level $v=v$," one may take a suitably weighted average of the two values of $\nu(\Pi, \Sigma)$ obtained by projecting from the two points of intersection of the level $v=v$ with the $U(r)$ curve of the Π state.] If B_v is the same for the Π and Σ states, as it should be in the ideal case of pure precession, then $\nu(\Pi, \Sigma)$ for $v=0$ is practically the same as $\nu_0(\Pi, \Sigma)$. In some cases, however, e.g. that of the $1s\sigma 2p\pi$, $^1\Pi$ state of H_2, the two quantities are far from being equal. In the case of a $^2\Pi$ state with a large case *a* doublet separation, a separate value of $\nu(\Pi, \Sigma)$ must be used for $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$.

In calculating γ for a $^2\Sigma$ state, the procedure is similar. The quantity $\nu(\Pi, \Sigma)$ is obtained by projecting upwards (or downwards) from the level $v=0$ (or $v=v$) of the $^2\Sigma$ state to the $U(r)$ curve (or curves) of the $^2\Pi$ state.—It should be noted that ν in *all* the equations used in this paper is to be taken as positive or negative according as the Π state is above or below the corresponding Σ state.

Hydrides with one outer p electron. The states listed in Tables I and II for H_2, BeH, MgH, ZnH, CdH, and HgH include a Σ and a Π state whose previously assigned electron configurations[23] might lead one to expect the case of pure precession. In each case, the most loosely bound electron is supposed to be in an np orbit, which when $\lambda=0$ ($np\sigma$) gives the Σ state, when $\lambda=1$ ($np\pi$)

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[23] Cf. R. S. Mulliken, Phys. Rev. **33**, 738 (1929); also F. Hund, Ref. 25 and elsewhere.

gives the Π state. In each case the values of p_0 and q_0 calculated for the Π state, and of γ_0 calculated for the $^2\Sigma$ state, agree remarkably well with the observed values. In nearly every case the calculated values are somewhat larger than the observed values, as would ordinarily be expected, since the ideal case of pure precession corresponds to the largest possible mutual influence of a Σ and a Π state. In CaH also we have a $^2\Sigma$ and a $^2\Pi$ state which show the same relations, together with other interesting features; discussion of this molecule will be postponed to a later section.

Observed values larger than calculated values may probably be attributed largely to the fact that Eqs. (7), (12), and (19) are really somewhat too simplified to give accurate results when ν is small and when at the same time there is a possibility of having very small values of $\nu(\Pi, \Sigma)$ for individual vibrational levels. In calculating, for instance, Λ-type doubling coefficients for a Π state, one should use a summation over all v values of the Σ state,[8] as in Eq. (5) except that here we assume that only one Σ state need be considered. Of course if all the vibrational levels of the Σ state are *above* the given v level of the Π state, Eqs. (7) and (12) should always hold well when we have pure precession. But if the zero level of the Σ state is *below* that of the Π state, then some of the terms in the summation may have very small $\nu(\Pi, \Sigma)$'s which may have an important effect on p_0 and q_0, even if BL_y is small. Usually these terms should tend to increase $|p_0|$ and $|q_0|$, since those ν's which have the same sign as the single weighted mean ν of Eqs. (7) and (12) should on the whole have larger BL_y's than those with opposite sign.

Associated with such cases as those under discussion there should be irregularities in the mode of dependence of $\Delta\nu_{dc}$ (and of T_c and T_d themselves) on v and on J (*perturbations*). A good example of a state showing irregular $\Delta\nu_{dc}$'s (larger than those calculated by Eq. 7) is the $1s\sigma 2p\pi$, $^1\Pi$ state of H_2. Similarly, except that here the case of pure precession is not at all approximated, the large and irregular $\Delta\nu_{12}$'s and the perturbed terms in the upper $^2\Sigma$ states of CdH and of HgH may be ascribed to their very close proximity to the higher vibrational levels of the $^2\Pi$ state.

The agreements of observed and calculated values of p_0, q_0, and γ_0 in Tables I and II even as to *order of magnitude* are very significant, since without a strong tendency toward the case of pure precession, even such agreements would not be expected. The actual observed agreements are so good as to leave little doubt that the case of pure precession is very often pretty closely approximated. This gives strong support to the views of Hund and of Mulliken, who have maintained that the "electron configurations" (or "electron orbits," or "wave-functions") in these molecules are really closely similar to those of the "united-atom" which would be obtained if the two nuclei were united, and radically different, in respect to one at least of the outer electrons, from the wave-functions which would exist if the molecule acted merely like two somewhat modified atoms. (The view that a molecule can nearly always be regarded as consisting merely of somewhat modified atoms seems to be widespread among those who have used the separated atoms as a starting point for the calculation of molecular properties).

An example will make the point clearer. We know beyond reasonable doubt[24] that the normal $^2\Sigma$ state and the $^2\Pi$ state of HgH are related to the states of their separated atoms as follows:

$$\text{Hg}, \cdots 6s^2, {}^1S + \text{H}, 1s, {}^2S \rightarrow \text{HgH}, {}^2\Sigma^+(+\,0.37 \text{ volts})$$

$$\text{Hg}, \cdots 6s6p, {}^3P + \text{H}, 1s, {}^2S \rightarrow \text{HgH}, {}^2\Pi(+\,1.8 \text{ volts}).$$

If in the molecule the H electron were still essentially a $1s$ electron, we could write

$$\text{HgH}, {}^2\Sigma^+: \cdots (6s\sigma^2)\sigma 1s; \quad \text{HgH}, {}^2\Pi: (6s\sigma 6p\pi)\sigma 1s.$$

The electron configurations of the Σ and the Π state would here be essentially the same except for the replacement of a $6s\sigma$ Hg electron present in the Σ state by a $6p\pi$ Hg electron in the Π state. But a $6s\sigma$ and a $6p\pi$ orbit, differing in l, are not related in such a way as to give pure precession, and the experimental evidence from the p_0, q_0, and γ_0 values in favor of pure precession could not be understood.

If, however, we suppose that the $1s$ orbit of the H electron has been completely changed when the molecule is formed, becoming a $6p\sigma$ electron in the case of the $^2\Sigma$ state, and a $6s\sigma$ electron in the case of the $^2\Pi$ state, we have

$$\text{HgH}, {}^2\Sigma^+: 6s\sigma^2 6p\sigma; \quad \text{HgH}, {}^2\Pi: 6s\sigma^2 6p\pi.$$

Now if the symbols $6s\sigma$, $6p\sigma$, $6p\pi$ really have quite definitely the meaning which they would have for the united-atom (Tl) under the influence of the electric field of a proton, we should expect the case of pure precession to be fulfilled, otherwise not. Comparison of the observed and calculated values of p_0, q_0, and γ_0 for HgH shows that pure precession is actually nearly fulfilled. In some of the other molecules of the same type, the agreement is even better than in HgH. It seems remarkable that in a molecular state like the $^2\Sigma$ normal state of HgH, whose energy of formation from its atoms is only 0.37 volt, the transformation of the wave-function from that of Hg+H toward that of the united-atom has been so complete as to give the observed close approximation to pure precession. It is also worthy of note that this thoroughgoing transformation takes place regardless of the fact that, according to conventional valence theory, no valence bond exists in this $^2\Sigma$ state of HgH.

Several interesting minor points, some of them giving considerable added support to the preceding conclusions, remain to be discussed.

Let us begin with the data on H_2. Here one notes an unusually large difference in the B_v values of the $^1\Sigma_u$ and $^1\Pi_u$ states which here give the pure precession. The $U(r)$ curve of the $^1\Sigma$ state lies rather close below that of the $^1\Pi$ state for small r values, and the two curves should come together at $r=0$. For large values of r the curves go far apart, but as $r \rightarrow \infty$, they finally come together again. An approximate diagram of these curves, and a partial ex-

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[24] Cf. R. S. Mulliken, Phys. Rev. **36**, 1449 (1930) for HgH curves, and E. Svensson, Zeits. f. Physik **59**, 349 (1930) for CdH. The curves given must, however, not be taken as more than roughly correct.

planation of their behavior, will be found in an article by Hund.[25] Probably the $^1\Sigma$ state departs markedly from united-atom conditions as r becomes fairly large, corresponding to a tendency of the $2p\sigma$ electron in H_2 to become a $1s$ electron (of $H^+ + H^-$), although actually it finally goes over as $r \to \infty$ into a 2-quantum electron of an H atom. For large r values, therefore, one cannot expect to find pure precession approximated, but if we calculate q_0 for the $^1\Pi$ state, for small values of v, we have r small enough so that conditions are near those of the united-atom. The fact that the observed q_0's are actually larger than those calculated for pure precession, and the irregularities in the $\Delta\nu_{dc}$'s as functions of v and K, have already been explained earlier in this section.

In BeH, γ_0 of the $^2\Sigma$ state is too small to measure, as would be expected, even for pure precession, from the calculated γ_0. In the $^2\Pi$ state (a good example of case b, with p_0 negligible), the observed q_0 is about two thirds the calculated, indicating that the case of pure precession is fairly well fulfilled. The mere fact that the observed q_0 is positive shows (cf. Eqs. 4, 5, 5a) that the $^2\Pi$ interacts principally with the $^2\Sigma$ state below it if, as is almost certain, this is $^2\Sigma^+$. (There is in all probability only *one* $^2\Sigma$ state below the $^2\Pi$). Similar remarks apply to MgH, ZnH, CdH, HgH. Of course $^2\Sigma^-$ states above the $^2\Pi$ would tend to make q_0 positive, but they are not often likely to be important.

The peculiarities in behavior of the rotational levels of the $^2\Pi$ state of BeH for large values of K, which Watson[26] attributed to a more or less complete uncoupling of an l vector, are here found to be explained by the variation of the moment of inertia with K. Thus the fact that the Λ-type doublet widths no longer increase in proportion to $K(K+1)$ for large K values can be explained in this way (cf. caption of Fig. 2). Likewise the fact that the rotational energy itself increases much less rapidly for large K values[26] than it would if given by $B_v K(K+1)$ alone is completely explained by the ordinary rotational stretching of the molecule, which is taken care of by added terms[27] beginning with $D_v K^2(K+1)^2$ as in Eq. (25). Thus there is no evidence in BeH of any large, much less of complete, rotational uncoupling of an l, even at the highest K values where the molecule is apparently approaching dissociation because of rotational instability. In making the calculations with Eqs. (22c) and (27), we have used $u^2 = 1.005 \text{x} 10^{-4}$, calculated from the experimental B and D values[27] $B_0 = 10.30$, $D_0 = -1.038 \text{x} 10^{-3}$.

According to Watson and Parker,[27] $\Delta\nu_{dc}(K)$ is negative in BeH for the lowest K values, for both T_1 and T_2 levels, then becomes positive and remains so (cf. experimental points in Fig. 2). According to Eq. (14), however, and in view of the small value of A/B which exists here, there is no possibility, for either T_1 or T_2 levels, that $\Delta\nu_{dc}$ can change sign at small K values (cf.

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[25] Cf. F. Hund, Zeits. f. Physik **63,** 719–751 (1930), especially pp. 741–2 and Fig. 5. Hund does not refer specificially to a tendency toward $H^+ + H^-$, although this is apparently involved in the tendency, which accounts for the low energy of this $^1\Sigma$ state at large r, of the $2p\sigma$ electron to become atomic $1s$.

[26] W. W. Watson, Phys. Rev. **34,** 1010 (1929); also Ref. 27, p. 173–4.

[27] W. W. Watson and A. E. Parker, Phys. Rev. **37,** 167 (1931).

theoretical curve in Fig. 2). It seems necessary to attribute the small observed negative values to experimental error.

Judging from the observed value of p_0 for the lower $^2\Pi$ state of MgH, the case of pure precession is well fulfilled there. The observed value of q_0 is, however, low, but the observed values of $\Delta\nu_{dc}$ are so small that the experimental p_0 and especially q_0 are not at all accurate. The upper $^2\Pi$ state of MgH, which is case *b*, has a relatively large positive value of q_0, suggesting that this $^2\Pi$ state stands approximately in the relation of pure precession to a $^2\Sigma^+$ state (. . . $3s\sigma^2 4p\sigma$) lying perhaps some 4000 cm^{-1} below it. Data on such a state seem not to be recorded in the literature.

For ZnH, CdH, and HgH, the data are accurate and extensive. As already noted, a relation of pure precession between the normal $^2\Sigma$ state and the $^2\Pi$ state is well fulfilled. The values of p_0 are accurately known experimentally, while those of q_0 are too small, relative to p_0, to be determined experimentally, except roughly in the case of ZnH. For $v=0$, the values of p_0 of $^2\Pi$ and of γ_0 of $^2\Sigma$ are nearly as large as those calculated for pure precession. The agreement with the calculated values is poorest in HgH, presumably because of the very small energy of dissociation of the $^2\Sigma$ state. The quantities p_0 and γ_0 are nearly equal, especially in ZnH and CdH, as they should be for pure precession.

In CdH and HgH we have data on p_0 and γ_0 for several values of v. According to Eqs. (26c) and (27b), p_0 and γ_0 should be proportional to B_v, but actually they decrease faster with v than B_v does (cf. observed and calculated values in Table II). This suggests that the case of pure precession is less and less well fulfilled as v increases. A natural explanation is that, as v increases, the electronic wave-functions become, on the average, more and more like those of two atoms, thus departing more and more (cf. discussion of HgH several paragraphs back) from the united-atom-like forms corresponding to pure precession.

Further evidence in regard to the effect of increased separation of the nuclei in causing departure from pure precession might be sought in a study of the $\Delta\nu_{dc}$'s for large values of J, where the molecule is considerably stretched by rotation. Here we use Eqs. (26), (27). In BeH we found that Eq. (27), with a varying q but *constant* q_0 holds fairly well up to rather large K values (Fig. 2). When plots for p and γ as functions of J and K are made for ZnH, CdH, and HgH, however, it turns out that for large J values not only p and γ but p_0 and γ_0 as well, diminish somewhat with increasing J (cf. Figs. 1, 3). Qualitatively, this can be accounted for by an increasing departure from pure precession as the molecule stretches and becomes more like two atoms.

We have so far not mentioned here the $^2\Sigma$ states which lie a short distance above the $^2\Pi$ states of ZnH, CdH, and HgH. These show large and often irregular $\Delta\nu_{12}$'s, corresponding mainly to large positive γ_0 values which, however, vary with K and v. An inspection of the $U(r)$ curves of these $^2\Sigma$ states[24] snows that they cross those of the $^2\Pi$ states of Table II. The crossing takes place in a region of low vibrational quantum numbers of the $^2\Sigma$ state and moderately high vibrational quantum numbers of the $^2\Pi$ states. The doubling in the $^2\Sigma$ states can probably be attributed mainly to interaction with these $^2\Pi$ levels.

The large size of the γ_0's is well explained by the smallness of the ν values without assuming that the BL_y's are at all comparable with those corresponding to pure precession. The irregularities of the $\Delta\nu_{12}$'s, together with observed irregularities of the term values T_1 and T_2 themselves, evidently result from the occurrence of unusually large interaction terms resulting from unusually small $\nu(\Pi, \Sigma)$ values for particular v, K values. In other words, we may speak of perturbations. The case is apparently rather similar to that in the red CN bands.[28] It deserves further study, although this is beyond the scope of the present paper.

Hydrides with two or more outer p electrons. In BH and AlH (Table I) there seems to be a fairly good approach to pure precession for the normal ($^1\Sigma^+$) state and the $^1\Pi$ state. In this case, unlike that of HgH, pure precession is equally to be expected for nearly-united-atom ($\cdots 3p\sigma^2, {}^1\Sigma$ and $\cdots 3p\sigma 3p\pi, {}^1\Pi$) and for separated atoms (Al, $\cdots 3p\sigma$, from ^2P, plus H, $1s$, and Al, $\cdots 3p\pi$, from ^2P, plus H, $1s$). In the nearly-united case, however, Eq. (7a) with $l=1$ applies (or if an L exists, Eq. 7 with $L=2$), while Eq. (7) with $l=1$ should apply in the separated case. The calculated q values are larger for the united-atom cases. The observed q values agree better with the separated-atoms case.

In OH there seems again to be a good example of pure precession. Particularly striking are the close agreement of p_0 with γ_0, and of the ratio p_0/q_0 with A/B_v, just as expected for pure precession. Nevertheless, the observed values of p_0, q_0 and γ_0 are decidedly less than the calculated ones. This case is interesting for the fact that A and ν are both negative, giving a positive p_0 and γ_0 but a negative q_0,—observed as well as predicted. The existence of a relation of pure precession between the $^2\Sigma$ and $^2\Pi$ of OH is perhaps assisted by the fact that there can be no other low-energy states; the next lowest states involve the displacement of a $2s\sigma$ electron to a $2p\sigma$ or $2p\pi$ orbit (which should require a large energy change), or of an electron to a 3-quantum orbit.

In HCl$^+$, whose electron configuration is analogous to that of OH, analogous relations exist for p_0, q_0, and γ_0, although the departures of the observed values from those calculated for pure precession are greater.

In CH we have a low $^2\Pi$ state (probably the normal state, unless perhaps a $^4\Sigma^-$ is lower), which from its electron configuration (cf. Table II) should apparently stand in the relation of pure precession to *three* other states, a $^2\Sigma^-$, a $^2\Delta$, and a $^2\Sigma^+$, all known empirically. The $^2\Delta$ state presumably cannot affect p_0 and q_0, but one might expect the latter to be determined by both the $^2\Sigma^-$ and the $^2\Sigma^+$ states. The $^2\Sigma^+$, since $\nu(\Pi, \Sigma)$ is negative, would according to Eq. (12) tend to make p_0 and q_0 negative, but the $^2\Sigma^-$, because it is Σ^- but at the same time has a negative ν, would tend to make p_0 and q_0 positive. One might expect to calculate p_0 and q_0 each as the sum of two contributions, a positive term from the $^2\Sigma^-$, largely cancelled by a negative one from the $^2\Sigma^+$. The observed values, however, do not agree with the values so calculated. Even

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[28] Cf. J. E. Rosenthal and F. A. Jenkins, Proc. Nat. Acad. Sci. **15**, 381 (1929).

greater discrepancies are encountered when one compares observed values of γ_0 for the $^2\Sigma^-$ and $^2\Sigma^+$ states with those calculated from Eq. (19). [For the $^2\Sigma^-$ state, $\gamma = -p = +2AB_v \cdots$]. But these results should not cause surprise, since as we have already seen (cf. discussion before and after Eq. 7a), the usual equations are not applicable to electron configurations like those present here in CH.

The relations in the $^2\Pi$ state of SiH are probably analogous to those in CH, but the $^2\Sigma$ levels are not yet known experimentally.

Molecules with a p electron belonging to one atom. In the case b' Π states of $He_2(^3\Pi)$, Li_2 and $Na_2(^1\Pi)$, we find the relation of pure precession well fulfilled toward certain neighboring states. The existence of this relation would not be expected from the electron configurations given in Table I. Although in each case the Σ differs from the Π state only in having a $p\sigma$ electron instead of a $p\pi$ electron, the principal quantum number n is not the same for the two, but is in each case one unit higher for the $p\sigma$. There can be hardly any doubt that this is true. In He_2, for example, we have already one $2p\sigma$ electron (a $2p\sigma 1s$, i.e. a promoted $1s$, electron); for the $^3\Sigma$ state here in question the other $p\sigma$ electron *must* according to the Pauli principle have a different value of n.

Apparently, however, this difference in n does not interfere seriously with the existence of "pure precession." But this is after all not difficult to understand. In the case of He_2, for example, the energy of the $\cdots 3p\sigma\, ^3\Sigma$ state is only a little above that of the $\cdots 2p\pi\, ^3\Pi$ state, and we believe that for $r \rightarrow \infty$ the electron in question becomes in both cases a $2p$ electron of one of the atoms, i.e., we have $3p\sigma 2p$ and $2p\pi 2p$. The small energy difference (much less than that between a 2- and a 3-quantum atomic orbit) indicates that the part of the wave-function corresponding to the $3p\sigma$ is really not much different from that which $2p\sigma$ would give in a helium atom. In other words, the electron orbits in the He_2 molecule are not very much different from those in the two atoms (He, $1s^2$+He, $1s2p$, ^3P) before union. Hence we get a strong interaction between the two states having $\cdots 3p\sigma 2p$ and $\cdots 2p\pi 2p$, agreeing well with the case of pure precession. Analogous relations exist in Li_2 and Na_2, although in these cases the $\cdots (n+1)p\sigma np$ is below the $\cdots np\pi np$, a fact which is faithfully reflected in the sign of q_0, and which is also signalized (as is reasonable) by a very close agreement of the q_0 values with those calculated for pure precession.

In the examples just discussed we apparently have the Λ-type doublet separations agreeing with those calculated for pure precession *because the wave-function of the molecule approximates that of two separate atoms*, whereas if the wave-functions were nearly as in the united-atom, we could not expect such agreement. This relation is the exact opposite of that found in molecules such as ZnH, CdH, HgH, where we saw that wave-functions resembling those of the separate atoms could not give pure precession, while wave-functions like those of the united atom do give it.

These results give strong support to the idea that among molecules there exist, for the outer electrons, examples of all stages of transformation of the electronic wave-functions from those of two separate atoms nearly to those of the united-atom. Examples of the first stage are found in loosely-bound molecules; an intermediate stage may be expected in stable states of firmly bound molecules like N_2; and the last stage is found in firmly-bound molecules with very unequal nuclei, notably among the hydrides.

Interpretation of the electron states of CaH. We have left the CaH molecule until the last, since it shows several interesting features. Beginning with the normal $^2\Sigma$ state, we notice that the observed γ_0 is only about one fourth that calculated on the assumption of a relation of pure precession between this state and the $^2\Pi$ state, whereas in the similar molecules ZnH, CdH, HgH, the observed γ_0 is not far below the calculated.

Furthermore, the observed p_0 and q_0 of the $^2\Pi$ state are negative, showing that this state interacts with a $^2\Sigma^+$ state *above* it. [The possible alternative of interaction with a $^2\Sigma^-$ state below it is too improbable from the standpoint of electron configurations.] Further, p_0 agrees well in value and has the same sign as γ_0 of a $^2\Sigma$ state which lies only 1320 cm^{-1} above the $^2\Pi$. Finally, the observed values of p_0, q_0, and γ_0 from the $^2\Pi$ and the upper $^2\Sigma$ (evidently $^2\Sigma^+$) states agree well with those calculated assuming a relation of pure precession between them with $l=1$ (cf. Table II). In view of the smallness of $|\nu(\Pi, \Sigma)|$, the agreement is surprisingly good (cf. the case of H_2 in Table I). The fact that B_v is practically the same for the $^2\Pi$ and $^2\Sigma^+$ states is no doubt important here, since it tends to cause $v=0$ of $^2\Pi$ to interact almost exclusively with $v=0$ of the $^2\Sigma^+$, and $v=0$ of $^2\Sigma^+$ with $v=0$ of $^2\Pi$.

In a previous paper,[23] it was suggested that the normal $^2\Sigma$ state of CaH is $\cdots 4p\sigma$, as in ZnH, and that the $^2\Pi$ and upper $^2\Sigma$ states are $\cdots 4p\pi$ and $\cdots 3d\sigma$. But in view of the relations stated in the preceding paragraphs, it seems evident that the upper $^2\Sigma$ is $\cdots 4p\sigma$, in which case it seems reasonable to assume that the normal $^2\Sigma$ is $\cdots 3d\sigma$. In the Ca atom, the $3d$ electron is almost as firmly bound as the $4p$, and apparently in CaH, the $3d\sigma$ is much *more* firmly bound than $4p\sigma$. This is presumably because $\lambda=0$ in $3d\sigma$ makes the $3d$ orbit penetrating. Even so, it is surprising that $\cdots 4p\sigma$ is above $\cdots 4p\pi$, but this may perhaps be attributed partly to a quantum mechanical repulsion between the states with $\cdots 3d\sigma$ and $\cdots 4p\sigma$. The fairly large γ_0 of the $\cdots 3d\sigma$ state may be attributable to the existence of a pure precession relation with a $\cdots 3d\pi$ state which probably lies above the $\cdots 4p\pi$. A quantum-mechanical repulsion between these two Π states may help to account for the fact that the $\cdots 4p\pi$ lies below the $\cdots 4p\sigma$. Possibly, however, the $\cdots 3d\pi$ lies below the $\cdots 4p\pi$ and is involved in some new infrared bands.[29]

As for dissociation products, there seems to be no reason to doubt that

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[29] B. Grundström and E. Hulthén (Nature **125**, 634, 1930) give data on the *C* system of bands, whose final level is the normal $^2\Sigma$ state of CaH. The observed hand-heads can be represented by the equation $\nu=28{,}290+(1423\ v' -24.7v'^2)-(1273\ v''-22.1\ v''^2.)$ The four observed vibrational levels of the lower state can be represented accurately by a linear function of v. Using a linear extrapolation as in the Birge and Sponer method, the energy of dissociation is 2.28 volts. Making a liberal allowance for actual departure of $G(v'')$ from linearity, 1.5 volts appears to be a reasonable value. Further data on CaH are given in a new paper by B. Grundström, Zeits. f. Physik, **33**, 235 (1931).

the $\cdots 4s\sigma^2 4p\pi$ and $\cdots 4s\sigma^2 4p\sigma$ both dissociate to give a normal H atom and a $\cdots 4s4p$, ^3P excited Ca atom, and that the $\cdots 4s\sigma^2 3d\sigma$ normal state gives a normal H and a normal Ca atom ($\cdots 4s^2$, ^1S). Since the interval $^2\Sigma$ (normal) to $^2\Pi$ is 1.78 volts, and the interval $^2\Sigma$(normal) to $^2\Sigma(\cdots 4p\sigma)$ is 1.94 volts, while the interval $4s^2$, ^1S to $4s4p$, ^3P in the Ca atom is 1.87 volts, it is evident that the energy of dissociation of the $^2\Pi$ state is only 0.09 volts more, that of the upper $^2\Sigma$ state 0.07 volts less, than that of the normal $^2\Sigma$. In other words, the energy of dissociation is nearly equal in these three cases. Its value for the normal state may be roughly estimated[30] as about 1.5 volts.

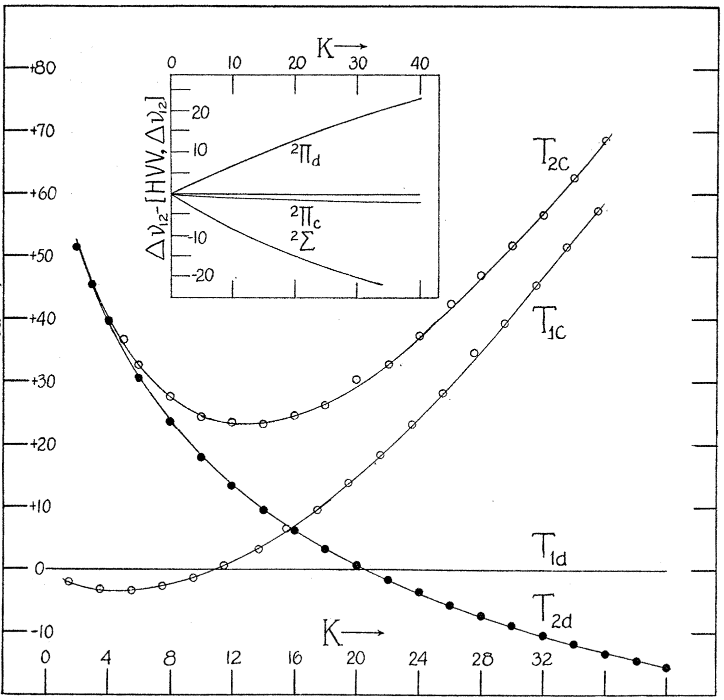

Fig. 4. Main figure: relative term values for the four sets of rotational levels T_{2c}, T_{1c}, T_{1d}, T_{2d} of the $^2\Pi$ state of CaH. All the term values are shown *relative* to the T_{1d} levels, $T_{1d}(J)$ being arbitrarily taken as zero. Inset: Spin doublet widths $\Delta\nu_{12}(K)$ for upper $^2\Sigma$ state of CaH (cf. also Fig. 3) and corrected spin doublet widths $\Delta\nu_{12}(K)-[\text{HVV}, \Delta\nu_{12}(K)]$ for the c and d sets of $^2\Pi$ levels. HVV, $\Delta\nu_{12}$ (K) means the doublet width which would be calculated according to Hill and Van Vleck's equation, taking only spin uncoupling into account. The *deviations* from this, $\Delta\nu_{12}-[\text{HVV}, \Delta\nu_{12}]$ represent secondary effects of l-uncoupling (cf. Eqs. 18, 19, 20c, 20d).

The $\cdots 4p\sigma$, $^2\Sigma$ state of CaH shows a peculiar curve for $\Delta\nu_{12}(K)$. It begins with nearly a straight line of slope -0.945, then for higher K values breaks over to another nearly straight line of slope -0.543 (cf. Fig. 3). In ordinary cases one finds a single straight line, $\Delta\nu_{12}(K)=\gamma(K+\frac{1}{2})$, up to high K values where γ begins to vary appreciably with K (cf. normal $^2\Sigma$ states of CdH and HgH in Fig. 3). In abnormal cases like the upper $^2\Sigma$ states of CdH and HgH, the irregular variations of $\Delta\nu_{12}$ with K are classified under the heading of perturbations, i.e. are ascribed to the influence of various individual levels whose $\nu(\Pi, \Sigma)$ happens to be very small. Very likely a similar explanation applies here, although perhaps a tendency toward case *c* for low K values might be held responsible.

The relative spacings of the four energy levels T_{1c}, T_{2c}, T_{1d}, T_{2d} as functions of K for the $^2\Pi$ state are interesting. They are shown in Fig. 4, which represents a revision of a somewhat similar figure by Watson, who has also given an interpretation of the uncoupling phenomena in this and the related $^2\Sigma$ state along the same general lines as here.[26,19] The positions of all the above four levels should be given by Eq. (9). This has not been tested directly here, but it has been shown that the doublet separations $\Delta\nu_{1dc}$ and $\Delta\nu_{2dc}$ are in accordance with Eq. (9),—cf. Eq. (14) and Fig. 2,—and that the doublet separations $\Delta\nu_{12d}(K)$ and $\Delta\nu_{12c}(K)$, also $\Delta\nu_{12}(K)$ of the $^2\Sigma$ state, show predicted behavior for high K values (cf. Fig. 4 inset, Eqs. 20c, 20d, and discussion following these equations).

The size of $\Delta\nu_{12}(K)$ in the $^2\Sigma$ state, and of $\Delta\nu_{12}(\text{corr.}) = \Delta\nu_{12}(K) - [\text{HVV}, \Delta\nu_{12}(K)]$ in the $^2\Pi$ states, permits ρ to be estimated somewhat directly, since we may expect these $\Delta\nu_{12}$ quantities to be equal to $A\rho$, where A is the known coupling constant obtained from the separation of the $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ levels at low J values. From the observed values of $\Delta\nu_{12}$ or $\Delta\nu_{12}(\text{corr.})$ at $K=33$, namely -22 for the $^2\Sigma$ state and $+20$ for the $^2\Pi^d$ state, together with the value $A = 80$, we conclude that the component of l along the direction of K is about 0.25. It seems rather remarkable, for such large uncoupling, that the Van Vleck formulas agree as well as they do with the experimental data. A careful re-examination of data on the Zeeman effect[19] of the $^2\Pi \rightarrow {}^2\Sigma$ and $^2\Sigma \rightarrow {}^2\Sigma$ bands of CaH in relation to the above conclusions might be of interest.

Molecules N_2^+, *BO*, *NO*, O_2^+. Data on these and similar molecules are not very abundant. The existing data give no clear indication of the existence of relations of pure precession between known states of these molecules. The absence of such relations is, however, in agreement with the probable electron configurations.

The opposite signs of p_0 and q_0 in the $^2\Pi$ state of BO are in agreement with the requirements of the theory for an inverted $^2\Pi$. The fact that p_0 is positive indicates, since A is negative, that the interacting Σ state or states lie above the $^2\Pi$, so as to make $\nu(\Pi, \Sigma)$ negative. The observed values of p_0 and q_0 indicate that if there is a relation of pure precession, the interacting $^2\Sigma$ state is a $^2\Sigma^+$ state lying somewhat higher than the upper of the two known Σ states. This state, which is unknown experimentally, should presumably have the electron configuration $\cdots 3p\sigma^2 2p\pi^3 3d\sigma 3d\pi$.

The fact that p_0 and q_0 have the same sign in the case of the $^2\Pi$ normal state of NO is in agreement with what the theory requires for a regular $^2\Pi$. The fact that p_0 and q_0 are positive[30] shows, since A is positive and $\nu(\Pi, \Sigma)$ is

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[30] The information that p_0 and q_0 are positive for the normal state of NO depends on the assumption that the $^2\Sigma$ state given in Table II (upper level of the γ bands) is $^2\Sigma^+$. This is very probable from a consideration of electron configurations. If, however, it were $^2\Sigma^-$, we should have to conclude that p_0 and q_0 are negative; and from this, that the $^2\Pi$ state interacts princi-

necessarily negative, that the $^2\Pi$ state interacts principally with a $^2\Sigma^-$ state, and not with the well known $^2\Sigma^+$ state listed in Table II (upper state of the γ bands). A $^2\Sigma^-$ state which should probably lie not very far above the $^2\Sigma^+$ state just mentioned, and whose electron configuration would correspond to a relation of pure precession with the normal $^2\Pi$ state, would be one with the configuration $\cdots 3d\sigma 2p\pi^4 3d\pi^2$. Such a state would probably have a large r_e like the upper $^2\Pi$ state, and so probably cannot be identified with the upper level of either the δ or ϵ bands of NO, one at least of which is $^2\Sigma$.

In the case of the O_2^+ bands it has been possible to determine the signs as well as the magnitudes of p_0 and q_0 if the very probable assumption is made that the normal state is $\cdots 3d\pi$, $^2\Pi_g$ as given in the table. Since in O_2 only levels symmetrical in the nuclei are present,[4] only positive rotational levels can be present in an even (g) state.[4] This requirement, in connection with the experimental data, suffices to determine the sign of $\Delta\nu_{dc}$. The result, that p_0 and q_0 are positive in the normal state of O_2^+, agrees with that observed[33] in NO, and may be taken as evidence in support of the even (g) character of normal O_2^+ and of the assigned electron configuration $\cdots 3d\pi$ for the normal states of O_2^+ and NO. In the case of the upper state of O_2^+, p_0 and q_0 are too small to determine. By analogy, it is very likely that p_0 and q_0 are also very small in the upper $^2\Pi$ state of NO. These coefficients cannot be directly determined for the upper $^2\Pi$ of NO from the available data, except that it can be said that, if p_0 of the lower state is $+0.015$, p_0 of the upper $^2\Pi$ is either $+0.03$ or ± 0.00. The analogy to O_2^+ now makes the latter value the more probable.

In conclusion, we take pleasure in acknowledging our indebtedness to Professor J. H. Van Vleck for helpful discussions and correspondence.

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pally with $^2\Sigma^+$ states above it. Thus whether we assume the upper level of the γ bands to be $^2\Sigma^+$ or $^2\Sigma^-$, we must conclude that it does not stand in a relation of pure precession to the $^2\Pi$ state. This conclusion in turn gives strong support to the original assumption that the $^2\Sigma$ state in question is not $^2\Sigma^-$, since a low $^2\Sigma^-$ could hardly be other than the one with the configuration . . . $3d\sigma 2p\pi^4 3d\pi^2$, which *should* stand in the relation of pure precession to the normal $^2\Pi$.