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REPORT ON NOTATION FOR SPECTRA OF DIATOMIC MOLECULES

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I. Introduction

FOR some time there has been much confusion and little agreement between different investigators in the field of band spectra, in respect to the symbols used for quantum numbers, spectroscopic terms, spectrum lines, and molecular constants as obtained from spectrum analysis. In the hope of remedying this situation, a number of those interested in the subject discussed the matter at Washington in April, 1929, and reached a tentative agreement on certain main points. The writer then undertook to obtain further discussion by correspondence, and for this purpose sent out on August 10 a circular letter embodying the results of the above discussion, somewhat modified and amplified as a result of subsequent experience. Copies of this letter were sent to about eighty spectroscopists. Many replies were received, and the matter was also discussed at the Faraday Society symposium on band spectra at Bristol in September.[1] On the basis of the foregoing, and of the replies to a second circular letter, sent out November 1, and of considerable additional correspondence with various individuals, the following report was prepared in tentative form, and copies were sent out with a third circular letter on March 15, 1930. After some changes based on replies to this third letter, the report is now presented.

In this report, the expression "it is recommended" is used in some cases, "it is suggested" in others. The *recommendations* represent the opinion, either active or acquiescent, of nearly everyone whose opinion has become known to the writer. They deal for the most part with important points about which definite conclusions have been reached. The *suggestions* are of a more tentative character. They deal in part with less important points and with matters where the need of general agreement is less imperative than in the case of the

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[1] "Molecular Spectra and Molecular Structure. A General Discussion held by the Faraday Society." Published in book form (Gurney and Jackson, 1930), also in Trans. Faraday Soc., pp. 611–950 (1929). In regard to nomenclature, cf. pp. 628–633 and pp. 768–772 and the Errata.

recommendations. In part they refer to topics which have not yet been sufficiently discussed to make definite recommendations.—In all the proposals given, the attempt has been made to take properly into account the varied needs of experimentalists and theorists.

The recommendations and suggestions given here have been made in such a way as to supplement and to be in harmony with those in the recent Report on Notation for Atomic Spectra.[2] In particular, the principle of using capital letters for quantum numbers representing angular momenta belonging to the molecule as a whole, and small letters for angular momenta of individual electrons, has been adopted. The recommendations apply for the most part only to diatomic molecules, but the manner of their extension to polyatomic molecules is in some cases obvious. Although a standard notation for polyatomic molecules would be very desirable, our knowledge of their spectra is as yet so undeveloped that it is perhaps best not to attempt this now. The only recommendation made here is that any notation chosen for polyatomic molecules be such as to harmonize with and supplement those used for atoms and diatomic molecules.

In addition to making recommendations and suggestions, opportunity has been taken to discuss a few matters of definition and nomenclature in regard to which misunderstandings have arisen or are likely to arise (Λ-type doubling, ρ-type multiplicity, band-origins, system-origins, "electronic," "vibrational," and "rotational" energy, etc.).

II. Quantum Numbers for Molecule as a Whole

General. For the *vibrational quantum number*, v *is recommended* to replace the hitherto usual symbol n.[3] The quantum number v has integral values (0, 1, 2, $\cdots$), the vibrational energy being given by $E_v=(v+\frac{1}{2})hc\omega_e+\cdots$ (in regard to ω_e, cf. Section V).

For the resultant angular momentum of any molecule, and its projection on an external field, the quantum number *designations* J and M *are respectively recommended* ($M=J, J-1, \cdots -J$). These designations are identical with corresponding designations for atoms.[4] The possible J values are 0, 1, 2, $\cdots$ for molecules with an even number of electrons, $\frac{1}{2}$, $1\frac{1}{2}$, $\cdots$ for those with an odd number. In certain coupling cases, J loses its meaning, and another quantum number K becomes prominent; in singlet states, J and K are identical, and may be used interchangeably: cf. p. 615 below.

Normal coupling: Hund's cases a and b. Before speaking in more detail about various quantum numbers associated with the angular momenta of

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[2] H. N. Russell, A. G. Shenstone, and L. A. Turner, Phys. Rev. **33**, 900 (1929).

[3] This change has been urged by a number of people, because of the increasing need of referring to v in the same paper, or even in the same sentence, in which n is used to designate the principal quantum number of an electron. The symbol v has already been used by J. H. Van Vleck (Phys. Rev. **33**, 477, 1929) and subsequently also by others.

[4] The use of J both for resultant *atomic* and for resultant *molecular* angular momentum is likely to cause some confusion. If its use were less well established for molecules (in the form j), J ought perhaps to be replaced by some other symbol, such as P (Hund proposed the symbol p). If this were done, M for molecules should also be replaced by another symbol.

electrons and nuclei in various coupling cases, it is desirable to review briefly the underlying theory.[5] We have always as angular momentum elements (1) the orbital angular momentum of the electrons, (2) their spin angular momentum, and (3) the angular momentum of the nuclear rotation. There are two coupling cases which may be regarded as normal,—cases *a* and *b* of Hund.

In both cases *a* and *b* we have for the resultant angular momentum of *spin* of the electrons a *quantum number* S, *exactly as in an atom.* Further, we have a quantum number [formerly called i_l, or σ_k or σ_l] for which *the designation* Λ *is here recommended*; $\Lambda h/2\pi$ represents (the numerical value of) the projection, on the electric axis of the molecule,[6] of the resultant orbital angular momentum of the electron system. The resultant orbital momentum itself is not at all rigorously quantized in molecules; nevertheless in comparing a molecule with the atom which would be obtained if its nuclei could be united, a resultant orbital *quantum number* L *may sometimes be assigned* as in the case of the atom; then Λ is the projection of L.[7] The possible values of Λ are $0, 1, 2, \cdots$.

In case *a* (possible only if $\Lambda > 0$) we have strong coupling of S to the electric axis, as a result of the magnetic field associated with Λ. Here the projection of S on the axis is a quantum number [formerly called i_s or σ_s] for which *the designation* Σ *is now recommended*.[7,8] Σ *has values* $S, S-1, \cdots -S$; it is considered to be a positive or negative quantity according as it is parallel or antiparallel to Λ. The numerical value of the algebraic sum of Λ and Σ is a quantum number [formerly called i, or σ] for which *the symbol* Ω *is recommended.* For given values of Λ and S, Ω has values $\Lambda+S$, $\Lambda+S-1$, $\cdots |\Lambda-S|$.[9] $\Omega h/2\pi$ is the total angular momentum parallel to the electric axis. This may be considered as combining vectorially with the angular momentum of the nuclei (a vector perpendicular to the electric axis)[10] to give the resultant angular momentum of the molecule (quantum number J, cf. Fig. 1). The possible values of J are $\Omega, \Omega+1, \Omega+2, \cdots$. The quantum num-

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[5] F. Hund, Zeits. f. Physik, **36**, 657 (1926). For further details, cf. R. S. Mulliken, Reviews of Modern Physics **2**, 60 (1930).

[6] *I. e.*, on the line joining the nuclei.

[7] More accurately, according to the new quantum mechanics, the resultant orbital angular momentum is $L^*h/2\pi$, where $L^* \equiv [L(L+1)]^{\frac{1}{2}}$; then Λ is the projection of L^* (each in units $h/2\pi$). Similarly the angular momenta associated with S, K, J, J^a, R, l, are, in units $h/2\pi$, really S^*, K^*, etc., and Σ is really the projection of S^*, etc. [A *recommendation* of the symbols L^*, S^*, etc. is not intended here.]

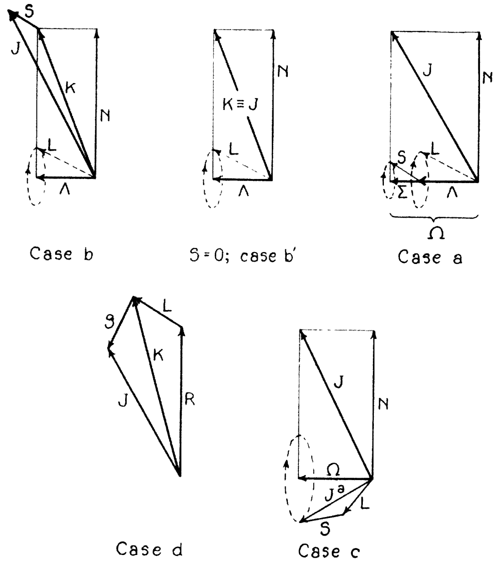
[8] Σ (Greek S) has been chosen,—after much discussion (the use of Greek X was at first proposed),—for the projection of S, in spite of the other common uses of this symbol, because its use here is analogous to that of Λ (Greek L) for the projection of L, and to the use of the symbols Σ, Π, Δ, $\cdots$, (Greek S, P, D, $\cdots$,) for states with $\Lambda = 0, 1, 2, \cdots$, as compared with S, P, D, for $L = 0, 1, 2, \cdots$.

[9] Usually, for a given Λ, a given value of Ω occurs only once, but if $S > \Lambda$, one or more values of Ω occur twice. For example, if we have $\Lambda = 1$, $S = 1\frac{1}{2}$, we have $\Omega = 2\frac{1}{2}, 1\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ corresponding to $\Sigma = 1\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -1\frac{1}{2}$.

[10] The component of angular momentum perpendicular to the electric axis, which in the text is for brevity called "the nuclear angular momentum," *is* really *mainly* angular momentum of the nuclei, but *also* includes small contributions from orbital (and spin, in cases *a* and *c*) angular momenta of the electrons. Cf. R. S. Mulliken, reference 5.

bers associated with the molecule as a whole in case *a* are thus v; L (sometimes, but never very rigorously quantized), Λ; S, Σ; Ω, J, M.

In case *b* we have Λ and S just as in case *a*, but S is not coupled to the electric axis, and there is no quantum number Σ. Case *b* exists whenever the magnetic field associated with Λ is too weak to couple S to the axis, a condition which is possible for any value of Λ, but which is automatically fulfilled when $\Lambda=0$. In case *b*, $\Lambda h/2\pi$ and the nuclear angular momentum[10] combine to give a quantized resultant (cf. Fig. 1). For the corresponding quantum number [formerly called p_l or j_k] *the designation K is now recommended.*[7] The possible values of K are $\Lambda, \Lambda+1, \Lambda+2, \cdots$. There is usually a small magnetic field in the molecule parallel to K, so that K and S form a resultant J (cf. Fig. 1).[7, 11] The quantity $J-K$ is often called ρ; ρ is approxi-



Case b S=0; case b′ Case a

Case d Case c

Fig. 1. Angular momentum vectors in Hund's cases *a*, *b*, *c*, *d*, expressed in units $h/2\pi$. In cases *a*, *b*, *c*, the angular momentum of the nuclear rotation[10] is represented by N, which is *not a quantum number*; in case *d* it is represented by the quantum number R. In all the figures, the horizontal base line perpendicular to N represents the direction of the electric axis (line joining the two nuclei). In cases *a* and *b*, Λ is shown as the projection of L, which is represented as precessing around the direction of Λ, i.e. around the electric axis; L is given by a dotted line to indicate that it is not rigorously quantized. In case *a*, Σ is shown as the projection of S, which is represented as precessing around the electric axis. In case *c*, Ω is shown as the projection of J^a (resultant of L and S), which is represented as precessing around the electric axis.[12a] In all cases, each pair of vectors which form a *resultant* must be thought of as precessing around the latter with a frequency which differs for each such pair. In each case, the only vector whose direction remains fixed is J. Precessing pairs are: Λ and N around J in the case $S=0$; Ω and N around J in cases *a* and *c*; Λ and N about K, and K and S about J, in case *b*; L and S about J^a in case *c*[12a]; R and L about K, K and S about J, in case *d*. [The use of N in Fig. 1 is not intended as a notation suggestion to be followed. In Ref. 5 the writer has used O where N appears here, and has used N with a somewhat different meaning than here.]

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[11] The combination of K and S to give J in a molecule is closely analogous to that of L and S to give J in an atom, and the designation K has been chosen with this in mind.

mately equal to the component of S parallel to J or K; ρ has sometimes been thought of as a quantum number, but this is incorrect. The splitting of a rotational level with given K into two or more levels differing in J might be referred to as ρ-type multiplicity (the expression "ρ-type doubling" has been in common use for the case $S=\frac{1}{2}$). This is, however, not recommended. Such an expression as "case b spin multiplicity" would be better.

In the presence of a "weak" external field J gives M. If the field is strong enough, however, the coupling of K and S is broken down (molecular Paschen-Back effect) so that J loses its significance, while K and S separately give projections for which *the designations* M_K and M_S (magnetic quantum numbers) *are recommended.* (M_K has as possible values, $K, K-1, \cdots -K$; M_S has values $S, S-1, \cdots -S$). Here $M=M_K+M_S$.

Sometimes the coupling of K and S in case b is practically zero; this situation can conveniently be distinguished as case b'. In case b', J is without significance. When $S=0$, cases a and b' become identical, as do K and J (cf. Fig. 1); here either K or J may be used to designate the resultant angular momentum; the designation K is the better in comparisons with case b' or b states with $S>0$, the designation J in comparisons with case a states.

Other coupling cases. In addition to cases a and b there are other less common cases which are nevertheless of sufficient importance to deserve consideration here. Hund's "case c" is an ideal limiting case in which L is assumed to be as rigorously quantized as in an atom, and, also, to be so strongly coupled to S as to give a quantized resultant as in an atom. *It is recommended that this resultant,* which in an atom would be called J, *be called* J^a in the case of a molecule.[12,12a] Λ and Σ here have no (quantum) meaning, but Ω is rigorously quantized, and is (the numerical value of) the projection of J^a on the electric axis. Ω has as possible values, $J^a, J^a-1 \cdots$ down to 0 or $\frac{1}{2}$ according as J^a is an integer or a half integer. Ω combines vectorially with the nuclear angular momentum to give J as in case a (cf. Fig. 1). In an external field J gives M.

In Hund's "case d," examples of which are found in the higher electron levels of H_2 and He_2, L is as rigorously quantized as in an atom,[13] but is unusually little influenced by the electric axis, so that it does not give a projection Λ on the axis. S also exists as usual, but it does not give a projection Σ. In case d the angular momentum of the *nuclei* by themselves is quantized; for this *the quantum number* R [same as Hund's p_r] *is recommended.* ($R=0, 1, 2, \cdots$). L is weakly coupled to R to give a resultant for which *the designa-*

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[12] The superscript a serves to indicate the relation to the *atomic* J.

[12a] There is also another, probably more important, form of case c in which L, J^a, and even S are not at all rigorously quantized, and in which Ω is the only rigorous electronic quantum number of the molecule. This case is found in loosely-bound molecular states formed by the union of two atoms one or both of which when alone has its own L and S strongly coupled to each other.

[13] Actually in He_2 the relations are more complicated: we have essentially case b for the inner electron or electrons, but case d for the excited electron, whose l is coupled in accordance with case d to an R which is really the K of the He_2^+ ion.

tion K is recommended; K has the values $R+L$, $R+L-1$, $\cdots |R-L|$.[14] K and S may now combine vectorially to give J, exactly as in case b (cf. Fig. 1.). In external fields we have, (1) in "weak" fields, a quantum number M as in previous cases; (2) in "strong" fields, M_K and M_S as in case b; (3) in stronger fields, M_R, M_L, M_S. If, as is true in H_2 and He_2, the coupling of K and S is very small, J is lacking in significance, just as in case b'. When $S=0$, we have $K\equiv J$. In such cases, we may speak of case d'. The quantity $K-R$ in case d', like $J-K$ in case b (cf. above) is frequently called ρ; ρ is here approximately equal to the component of L parallel to K or R; it is not a quantum number.

As a variation on case d, we might have "case e," in which L and S are coupled to give a J^a as in case c, while J^a and R give a resultant J.

III. TERM SYMBOLS

For coupling cases approximating Hund's a or b, or intermediate between them, the use of the *symbols* Σ, Π, Δ, Φ, Γ, H, $\cdots$ *to indicate* $\Lambda=0, 1, 2, 3, 4, 5, \cdots$ *is recommended.* [Until recently the symbols $S, P, D, \cdots$ have been used for $\Lambda=0, 1, 2, \cdots$ as well as for $L=0, 1, 2, \cdots$.] In coupling cases resembling or tending toward case d, or also in theoretical discussions where a molecule is to be compared with the atom obtainable by uniting its nuclei, L values can be indicated by using the symbols $S, P, D, \cdots$ for $L=0, 1, 2 \cdots$. To indicate both L and Λ, symbols such as $P\Sigma$, $D\Pi$, etc., may be used.

The multiplicity (equal to $2S+1$) should be indicated, as in the case of atoms, by a superscript at the left, as $^1\Sigma$, $^2\Pi$, etc. In coupling cases approximating case a, *it is recommended that the value of* $\Lambda+\Sigma$ be indicated by a *subscript at the right*.[15] (For singlet states, however, no subscript is needed, since $\Sigma=0$ always, so that $\Lambda+\Sigma=\Lambda$; while for case b states no subscript is possible, since a quantum number Σ does not exist). Examples, $^1\Sigma$, $^1\Pi$, $^2\Sigma$, $^3\Delta_2$, $^4\Pi_{2\frac{1}{2}}$, $^4\Pi_{1\frac{1}{2}}$, $^4\Pi_{\frac{1}{2}}$, $^4\Pi_{-\frac{1}{2}}$.[16]

There are two kinds of Σ states, which differ in respect to the symmetry of their wave-functions with respect to a plane through the line joining the nuclei. In the one kind the *electronic factor* of the wave-function ψ (corresponding to the motion of the electrons with reference to the nuclei) is unchanged on reflection in such a plane, in the other kind it changes sign.

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[14] K in case d has a somewhat different physical meaning than K in case b, but is exactly like the latter in that it combines with S to give J. Further, there is a one to one correspondence between the K values in case d and those in case b, and K is quantized throughout the whole range of intermediate cases.

[15] The recommendation that the value of $\Lambda+\Sigma$, rather than that of Ω, be used for the subscript in molecular multiplets is based on the fact that when $S>\Lambda$, $\Lambda+\Sigma$ takes on negative as well as positive values. In such cases [none of which, however, have yet been observed] it would not suffice to specify Ω, since $\Omega=|\Lambda+\Sigma|$. In $^4\Pi$ states, for example, we should have $\Omega=\frac{1}{2}$ for both $^4\Pi_{\frac{1}{2}}$ and $^4\Pi_{-\frac{1}{2}}$.[9] In this connection it may be well to remind the reader that in molecular multiplets, in contrast to many cases of atomic multiplets with $L>0$, the full multiplicity is always developed whenever $\Lambda>0$. For example, the molecular level $^4\Pi$ is quadruple (cf. reference 9) while the atomic ^4P is only triple.

[16] For subscripts which are multiples of $\frac{1}{2}$, either of the two forms such as $\frac{3}{2}$ or $1\frac{1}{2}$ may be used, but the second form ($1\frac{1}{2}$) is preferable for typographical reasons (cf. reference 2, p. 900).

It is recommended that these be distinguished, when one wishes, by calling them respectively Σ^+ and Σ^- states.[16a] [The designations Σ^+ and Σ^- respectively correspond to Σ and Σ' of Wigner and Witmer.[17,18]].

In the case of homonuclear molecules (molecules composed of atoms whose nuclei are identical in charge and mass), any electron state may be either "odd" or "even."[19] An electron state of a homonuclear molecule is said to be *odd* if the *electronic factor* of ψ changes sign on reflection in the midpoint of the line joining the nuclei, *even*, if it does not change sign.[19,19a] *It is recommended* that the odd or even character of an electron state, *when known*, and *if desired*, be indicated by a subscript at the right of the electronic term symbol. The subscripts *g* (German *gerade*) for even terms and *u* (German *ungerade*) for odd terms are recommended.[20] Examples, ${}^1\Sigma_g$, or ${}^1\Sigma_g^+$, or ${}^1\Sigma_g^-$, ${}^2\Sigma_u$;

[16a] Corresponding to the frequently used empirical designations such as Π_b and Π_a (cf. Section VI, Fig. 2, etc.), theoretical designations such as Π^+ (even terms[19a] when K is even) and Π^- (odd terms when K is even) might be introduced, in analogy to Σ^+ and Σ^-.

[17] E. Wigner and E. E. Witmer, Zeits. f. Physik, **51,** 859, 1928. In Σ^+ states the rotational levels with even values of K are "even" or "positive," those with odd K are "odd" or "negative," while in Σ^- states these relations are reversed.[19a]

[18] Wigner and Witmer's use of Σ where Σ^+ is proposed here is obviously undesirable, since the symbol Σ is needed to imply *merely* $\Lambda = 0$ in cases where one cannot, or does not wish to, decide between Σ^+ and Σ^-, as well as in general discussions. Wigner and Witmer's use of Σ' where Σ^- is proposed here is undesirable because of the frequent use of the prime ($'$), in the analysis of spectra, to denote the upper of two energy levels.

[19] The use of "odd" and "even" in this sense was introduced by Hund. Cf. the useful summary by W. Weizel, Zeits. f. Physik, **54,** 324–6 (1929).

[19a] The words even and odd are applied by Kronig, in a sense different from that used by Hund,[19] to the *complete* ψ function of any molecule, homonuclear or heteronuclear; a molecular term is odd or even in this sense according as its ψ function does or does not change sign on reflection in the origin of coordinates; this definition is the same as that which holds for odd and even atomic terms. Instead of "even" and "odd" Wigner uses "positive" and "negative" for atomic terms, and Wigner and Witmer (l.c., Ref. 17) for molecular terms.

In speaking of molecular terms, the designations "even" and "odd" (which may be abbreviated *g* and *u*, as in Fig. 2) may be preferred to "positive" and "negative" on two grounds: (1) they were introduced earlier (R. de L. Kronig, Zeits. f. Physik, **50,** 351, 1928), and (2) they refer to the same properties which in atoms are generally described by "even" and "odd." But "positive" and "negative" (which may be abbreviated + and −) may be preferred on other grounds: (1) they avoid possible confusion with the earlier-introduced and equally well-founded use of "even" and "odd" in another sense for electronic terms;[19a] (2) they avoid the confusing situation that molecular levels with even, or with odd, K values may be either "even" or "odd." In Fig. 2 and elsewhere in this report, "even" and "odd" are used, but the writer now intends personally to use "positive" and "negative."

[20] In the report on line spectra (reference 2), it was suggested that a superscript° (degree mark) always be used for odd terms, and *no* superscript for even terms. It may be that this precedent should be followed, although "odd" and "even" do not have just the same meaning here as in atoms. But this would hardly be feasible anyway in molecular spectra, since in some cases we do not yet *know* whether a term is even or odd. Further, there are many purposes for which the odd or even character is a matter of indifference, and it is desirable in such cases to be able to drop the superscript, without thereby implying that the term is even. The choice of *g* and *u* in preference to the English *e* (even) and *o* (odd) is based mainly on the fact that *e* is often used as a subscript for other purposes, as in E_e and r_e, while *o* is easily confused with zero.

The choice of the subscript position is governed by the fact that *g* and *u* are sometimes

${}^2\Pi_{\frac{1}{2}g}$; ${}^3\Pi_u$. [The designations Σ_g^+, Σ_u^+, Σ_g^-, Σ_u^-, Π_u, Π_g, Δ_g, Δ_u, etc. as here proposed, respectively correspond to Σ_+, Σ_-, Σ'_+, Σ'_-, Π_+, Π_-, Δ_+, Δ_-, etc. of Wigner and Witmer.]

The term symbols just recommended are of course not sufficient to identify completely the electronic state of a molecule. This purpose can be accomplished by the use of an identifying symbol of an empirical character, as for example A, B, X, a, etc.; or by the use of a symbol describing the electron configuration (cf. section IV, below.) *It is recommended* that such symbols be placed before the symbol giving S, Λ and Σ, as in the following examples: $A\ {}^3\Pi_2$; $X\ {}^1\Sigma$; $1s\sigma^2 2p\sigma 2s\sigma\ {}^3\Sigma$ (if the meaning is clear from the context, this last may be abbreviated to $2s\sigma\,{}^3\Sigma$ or $2s\ {}^3\Sigma$). These and similar designations can be adapted to the individual case, and varied to suit the need of experimentalist and theorist.

If one desires to express the relation of a molecular electronic state to the states of its atomic dissociation products, it is suggested that designations such as the following be used: $X\ {}^1\Sigma({}^2S+{}^2P)$. Here ${}^2S$ and ${}^2P$ represent the states of the two atoms. If desired, the electron configurations of atoms and molecule can also be given.

Some writers have used a superscript number, appended to the electronic term symbol, to indicate v. Example, ${}^3\Sigma^2$, for $v=2$. It is suggested that this practice be avoided if possible, and that simpler, although longer, expressions such as "the level $v=2$ of ${}^3\Sigma$" be used. In case, however, a necessity is felt for including v in the term symbol, it is suggested that this be given as a superscript *in parentheses to indicate* that it represents an element foreign to the rest of the symbol. Examples, ${}^3\Sigma^{(2)}$; ${}^3\Sigma_g^{-(2)}$.

If one needs to give the rotational quantum number (K or J) as well as v, it may be given in parentheses as in the following example: ${}^3\Sigma^{+(1)}$ (10), for $v=1, K=10$.

IV. QUANTUM NUMBERS FOR INDIVIDUAL ELECTRONS; ELECTRON CONFIGURATIONS

The designation Λ was recommended above as the quantum number for the component, parallel to the electric axis, of the resultant orbital angular momentum of the entire electron system. The *designation* λ *is now recommended* [to replace the former designation i_{l_τ} or σ_{l_τ} or σ_{k_τ}] for the corresponding quantum number for an *individual electron*.[21] It is *recommended* further

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needed for *individual electrons* (cf. Section IV below), as in $\sigma_g, \sigma_u, \pi_g$, etc., where the superscript position would lead to awkwardness in the symbols for electron configurations. For example, $\sigma_g{}^2\sigma_u{}^2\pi_u{}^4$ is much less awkward than $\sigma^{g2}\sigma^{u2}\pi^{u4}$. It is also preferable in such symbols as ${}^2\Sigma_g^+$, ${}^2\Sigma_u^{+(3)}$, etc. In cases such as ${}^2\Pi_{\frac{1}{2}g}$ it is not so good, but also not very bad, and furthermore, one is usually not interested in the $\frac{1}{2}$ and the g at the same time, so that one will usually write just ${}^2\Pi_{\frac{1}{2}}$ or else ${}^2\Pi g$, depending on the nature of the discussion.

[21] The quantization leading to the assignment of λ values for individual electrons is rigorous only to the extent that the interactions of the electrons with one another can be replaced by an axially symmetrical electric field. Ordinarily, however, the assignment of individual λ *values in molecules* should be about as justifiable as the assignment of individual l *values in atoms.*

that electrons having $\lambda=0, 1, 2, 3, 4, 5, \cdots$ be respectively *designated* σ, π, δ, ϕ, γ, η, $\cdots$ electrons. [These were formerly named $s, p, d, \cdots$ electrons by the present writer, although not with the same meaning as $s, p, d, \cdots$ in atoms.]

Under some circumstances quantum numbers n, l, and s can also be assigned to the individual electrons in a molecule, just as to those in an atom. In Hund's case d these quantum numbers have practically the same meaning as in an atom (examples, excited orbits of series electron in H_2, He_2).[22] Ordinarily, however, n and l are not at all rigorous quantum numbers and have a definite meaning only in terms of some ideal limiting case, such as that of the atom which would be obtained ("united-atom") if one could unite the two nuclei of the molecule.[22,23] To designate the values of l in a molecule the symbols $s, p, d, \cdots$ *are recommended* for $l=0, 1, 2$, just as in the case of an atom. When n, l, and λ are all to be indicated for an electron, *symbols such as* $2p\sigma$, $3s\sigma$, $3p\pi$, $4d\sigma$, $\cdots$ *are recommended*; the number represents n. [In the notation formerly used by the present writer, the equivalents of these symbols are $2s^p$, $3s^s$, $3p^p$, $4s^d$, $\cdots$ respectively.][24] When several electrons $(1, 2, 3, \cdots)$ are present, their several values of n, l, λ can be indicated, if desired, by numerical subscripts, as $l_1, l_2, \cdots \lambda_1, \lambda_2$, etc.

The quantum number λ represents the projection of l on the electric axis of the molecule.[7] Ordinarily any λ is considered a positive quantity, but in a molecule with several electrons some of the λ's must be considered as having a negative sign. Λ is then the algebraic sum of the individual λ's. Those individual λ's whose direction is opposite to Λ are regarded as having a negative sign.

Even when the assignment of an l value to an electron has little meaning there is still, *in symmetrical molecules*, a definite distinction between *odd* and *even* states of an electron. Thus one may speak of σ_g, σ_u, π_u, π_g, $\cdots$ etc. electrons. Insofar as an l can be assigned, an even value of l always gives an even type of electron (σ_g, π_g etc.), and an odd value of l an odd type.—In a similar way, the even or odd character of the resultant electron state of a symmetrical molecule is determined, like that of an atom, by the (*arithmetic*) sum of the individual l values. If this sum is even, the term is even (Σ_g, Π_g, $\cdots$ etc.), and conversely.

Often one may wish to indicate not the "united-atom" values of l and n for an electron, but the values of l and n which the electron would have if the molecule were separated into its atoms. For this purpose, symbols such as $\sigma(1s)$, $\sigma_g(2p)$, $\pi(2p)$, etc., are suggested. Here the symbol σ or π gives the

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[22] For the series electron in H_2 and He_2, most of the orbits are large compared with the distance between the nuclei, so that "united-atom" conditions are closely approximated.

[23] In terms of spherical coordinates (r, θ, φ) as in the ideal limiting case of the "united-atom," l is defined as $n_\theta+n_\phi$, where n_θ and n_ϕ are quantum numbers associated with θ and φ. In terms of elliptical coordinates (ξ, η, φ), as in another ideal limiting case where the electrons move under the influence of two point charges (as in H_2^+), l is defined as $n_\eta+n_\theta$ ($\eta=$ const. is a hyperboloid of revolution).

[24] The symbols $2s^p$ etc. were introduced by the present writer (Phy. Rev. **32**, 186, 1928); $2p\sigma$, etc. by F. Hund. (Zeits. f. Physik, **51**, 759, 1928).

value of λ for the electron in the molecule, while the symbol in parentheses describes the state of the electron as it would exist in one of the atoms on dissociation of the molecule.

Electron configurations. A rather complete description of the state of a molecule is possible if the term symbol, which gives the quantum numbers associated with the molecule as a whole, is preceded by a set of symbols giving the electron configuration. Examples: $1s\sigma^2 2p\sigma^2 2s\sigma^2 2p\pi^3\ {}^2\Pi$; or more briefly, $\sigma^2\sigma^2\sigma^2\pi^3\ {}^2\Pi$; or, if the molecule is symmetrical, $\sigma_g^2\sigma_u^2\sigma_g^2\pi_u^3\ {}^2\Pi_u$. The electron configuration designations used here are similar to those used in line spectra. Such a symbol as $1s\sigma^2$ really means $(1s\sigma)^2$, i.e., it indicates the presence of two $1s\sigma$ electrons; while σ^2 indicates any two σ electrons of identical type (equivalent σ electrons). The order in which successive symbols are written is that of decreasing firmness of binding.—Such a symbol as $\sigma^2\sigma^2\sigma^2\pi^3$ rather than $1s\sigma^2 2p\sigma^2 2s\sigma^2 2p\pi^3$ is often to be preferred, since the assignment of definite n and l values is usually rather lacking in meaning. The symbol $\sigma^2\sigma^2\sigma^2\pi^3$ signifies the existence of three different kinds of σ electrons without attempting to describe them in detail.

V. SYMBOLS FOR MOLECULAR CONSTANTS

The energy E of a diatomic molecule is commonly written as a sum of three parts (for exact definitions, cf. Section VI):

$$E = E_e + E_v + E_r \tag{1}$$

Here E_e is the "electronic energy," E_v is the "vibrational energy," and E_r is the "rotational energy."

For the energy of a molecule in a singlet state[25] we had according to the old quantum theory (using, however, the new symbols v and J in place of n and j)[26]

$$E = E_e + hc[\omega_0 v - x\omega_0 v^2 + y\omega_0 v^3 + \cdots] \\ + hc[B_v(J^2 + \text{const.}) + D_v J^4 + F_v J^6 + H_v J^8 + \cdots] \tag{2}$$

Here the first expression following E_e represented E_v, the second E_r. In Eq. (2), we had

$$B_v = B_0 - \alpha v + \gamma v^2 + \cdots, \text{ where } B_0 = h/8\pi^2 c\mu r_0^2 = h/8\pi^2 cI_0. \tag{3}$$

Also,

$$D_v = D_0 + \beta v + \cdots, \text{ where } D_0 = -4B_0^3/\omega_0^2. \tag{4}$$

In Eqs. (2)–(4), the subscript zero attached to a coefficient implied that this coefficient corresponded to $v = 0$. *At the same time,* since the energy of vibra-

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[25] The "*const.*" in (J^2+*const.*) depends on the electronic motions (cf. R. S. Mulliken, ref. 5, Eq. (29)). Small constants should also be added to the terms in J^4, etc.; and other small terms should be added.

[26] The notation used for the coefficients in Eqs. (2)–(4) etc. is mainly that which is now most usual. Instead of ω_0 one often finds ν_0 or ω^0; instead of $D_v, -\beta$. The designation $y\omega_0$ in Eq. (2) and γ in Eq. (3) are not in common use, but have been introduced here to supply an existing lack. No *recommendation* of this use of y and γ is intended here.

tion was supposed to be zero when $v=0$, it implied a molecule with stationary nuclei in a state of *equilibrium*. Thus $c\omega_0$ was supposed to represent the frequency of vibration for $v=0$, and so the limiting frequency for infinitesimal amplitudes. Similarly B_0 referred to $v=0$, and so supposedly to a molecule in equilibrium; and the quantities r_0 and I_0 calculated by means of Eqs. (3) likewise were supposed to correspond to a molecule in equilibrium.

According to the new quantum theory, however, Eqs. (2)–(4) must be replaced by equations of the following form:[26a]

$$E = E_e + hc\{\omega_0(v+\tfrac{1}{2}) - x\omega_0(v+\tfrac{1}{2})^2 + y\omega_0(v+\tfrac{1}{2})^3 + \cdots\} + hc\{B_v[(J+\tfrac{1}{2})^2 + \text{const.}] + D_v(J+\tfrac{1}{2})^4 + \cdots\} \quad (2a)$$

$$B_v = B_0 - \alpha(v+\tfrac{1}{2}) + \gamma(v+\tfrac{1}{2})^2 + \cdots, \text{where } B_0 = h/8\pi^2 c\mu r_0^2 = h/8\pi^2 cI_0 \quad (3a)$$

$$D_v = D_0 + \beta(v+\tfrac{1}{2}) + \cdots, \text{ where } D_0 = -\ 4B_0^3/\omega_0^2. \quad (4a)$$

If one assumes the validity of Eqs. (2a)–(4a) one gets somewhat *different numerical values* for E_e, ω_0, x, B_0, r_0, I_0, etc. than if one assumes Eqs. (2)–(4). In the literature most of the recorded values are based on Eqs. (2)–(4), although in some recent articles Eqs. (2a)–(4a) have been used as a basis of calculation. Thus the same symbols are now being used in different articles in two different ways, with resulting confusion on the part of the reader.

To remedy this situation a *revision of nomenclature is suggested*, at least for discussions dealing with the analysis of band spectra, such that Eqs. (2a)–(4a) are replaced by the following Eqs. (2c)–(4c).[26,26a,27,28] At the same time, equations of the form of Eqs. (2)–(4), except for the substitution of $(J+\frac{1}{2})^2$ for J^2, may usefully be retained (Eqs. 2b–4b).[29] Eqs. (2b)–(4b) represent the more useful form for the empirical description of spectra, Eqs. (2c)–(4c) for the analysis of the isotope effect and for the theoretical application of band spectrum data as in the construction of $U(r)$ curves (cf. second paragraph following).

$$E = E_0 + hc[\omega_0 v - x\omega_0 v^2 + y\omega_0 v^3 + \cdots] + hc\{B_v[(J+\tfrac{1}{2})^2 + \text{const.}] + D_v(J+\tfrac{1}{2})^4 + \cdots\} \quad (2b)$$

$$B_v = B_0 - \alpha v + \gamma v^2 + \cdots \quad (3b)$$

$$D_v = D_0 + \beta v^2 + \cdots \quad (4b)$$

$$E = E_e + hc\{\omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 + y_e\omega_e(v+\tfrac{1}{2})^3 + \cdots\} + hc\{B_v[(J+\tfrac{1}{2})^2 + \text{const.}] + D_v(J+\tfrac{1}{2})^4 + F_v(J+\tfrac{1}{2})^6 + \cdots\} \quad (2c)$$

[26a] Although the form $(J+\frac{1}{2})^2$ is used here, it is immaterial to the present discussion whether this or the rival form $J(J+1)$ is used.

[27] The use of the symbol E for energy, as in E and E_0, although it seems desirable, is not definitely included in the recommendations made here.

[28] The coefficients of Eqs. (2b)–(4b) are related to those of Eqs. (2c)–(4c) as follows: E_0 (Eq. 2b) $=E_e$ (Eq. 2c) $+hc\ [\frac{1}{2}\omega_e-(1/4)\ x_e\omega_e+(1/8)\ y_e\omega_e+\cdots]$; $\omega_0=\omega_e\ [1-x_e+(3/4)\ y_e+\cdots]$; $x\omega_0=\omega_e[x_e-(3/2)\ y_e+\cdots]$; $y\omega_0=\omega_e\ (y_e+\cdots)$; etc.

[29] The quantities r_0 and I_0 calculated as in Eq. (3) are no longer of much interest, since they are not empirical coefficients, nor have they the theoretical importance of r_e and I_e.

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \cdots, \text{ where}$$
$$B_e = h/8\pi^2 c\mu r_e^2 = h/8\pi^2 cI_e \qquad (3c)$$
$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) + \cdots, \text{ where } D_e = -\,4B_e^3/\omega_e^2. \qquad (4c)$$

The coefficients ω_e, B_e, etc. and the quantities I_e and r_e (and E_e) refer to a molecule with stationary nuclei in equilibrium; such a molecule, however, in contrast to the state of affairs in the old quantum theory, would *not* at the same time have $v=0$. B_0, D_0, E_0, etc., refer to a molecule with $v=0$.[29]

For the *energy of dissociation* of a molecule, the symbol D has been widely adopted. To be accurate, one must distinguish D_e, the energy of dissociation for the imaginary case of a molecule with nuclei stationary at the distance r_e; and D_0 or D, the energy of dissociation from the actual lowest energy level of the molecule ($v=0$). The values of D for various states of a molecule may be conveniently distinguished by putting identifying designations in parentheses, as $D(X)$ or $D(X\,{}^1\Sigma)$; $D(A\,{}^3\Pi)$; etc. In all cases the symbol D should stand for the energy of dissociation alone, and should not include, in the case of an excited electron state, the energy of excitation.

If the energy of a molecule in a definite electron state, with nuclei held stationary, is expressed as a function $U(r)$ of the distance between the nuclei, then $E_e \equiv U(r_e)$, while the dissociation energy $D_e \equiv U(\infty) - U(r_e)$. Also, $4\pi^2\mu c^2\omega_e^2 = (d^2U/dr^2)_{r=r_e}$

It may eventually be worth while to discard the heterogeneous and cumbersome set of symbols B_v, D_v, α, β, ω_e, $x_e\omega_e$, etc.[26] in favor of a simpler set. If, or when, this is done, the double use of D for heat of dissociation and for the coefficient of $(J+\frac{1}{2})^4$ might well be done away with. One might perhaps use d_v instead of D_v in the E_r expression (also, for consistency, f_v instead of F_v and possibly also b_v instead of B_v). This would, however, interfere with the possible future use of a, b, c, $\cdots$ in place of ω_e, $x_e\omega_e$, $y_e\omega_e$ $\cdots$ in Eq. (2c), or perhaps better in place of ω_0, $x\omega_0$, $y\omega_0$, $\cdots$ in Eq. (2b); a, b, $\cdots$ have already often been used in this way.

VI. DESCRIPTION AND ANALYSIS OF SPECTRA

Term designations. In the analysis of spectra, one is usually concerned with the determination of energy values (E) or term-values (E/hc) through the use of the relation $\nu = (E'-E'')/hc$. The prime (′) and double prime (″) are used merely to indicate that $E' > E''$.[27] *It is recommended that the prime and double prime* be always used in a similar manner when one wishes to distinguish the *upper* and *lower* of two energy levels involved in the production of the lines of a band spectrum, and that this method be applied to all quantum numbers and coefficients pertaining to these energy levels. In discussing spectra, it is best to avoid where possible the expressions "initial" and "final" levels, since in terms of E' and E'' these have opposite meanings in absorption and emission spectra.

In the analysis of spectra, it is convenient to have a symbol to denote term-values. *It is suggested* that T be used for this purpose ($T \equiv E/hc$).[30] For

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[30] The symbol F has sometimes been used for E/hc. (The present writer has in fact used this, and also F^{el} for E_e/hc, F^v for E_v/hc, and F^r for E_r/hc). But F has *usually* been used

the upper and lower levels involved in the production of a spectrum line, T' and T'' would be used.

In dealing with the analysis of a particular spectrum, the symbol T, followed by the rotational quantum number designation in parentheses, also the vibrational quantum number, if desired, as a superscript in parentheses, is suggested as a convenient symbol. Examples: $T(8)$, $T^{(2)}(8)$; also, $T_1(8\frac{1}{2})$, $T_{2a}(7\frac{1}{2})$, $T_a(9)$, etc., using numerical and literal subscripts in a manner to be discussed below in connection with the symbol F(cf. paragraphs following Eq. (7)).

For some purposes it is extremely convenient to have separate symbols for "electronic terms" (E_e/hc), "vibrational terms" (E_v/hc), and "rotational terms" (E_r/hc). *It is suggested* that the symbols G and F be used for vibrational and rotational terms respectively.[30] For electronic terms the symbol T_e *is suggested.* Thus we have, paralleling Eq. (1),

$$T = T_e + G + F. \tag{5}$$

Definitions of electronic, vibrational, and rotational energies and terms. It is important to define with some care the quantities F, G, and T_e, or the corresponding quantities E_r, E_v, and E_e. The following definitions appear to be unambiguous.

(1) The energy E_r is the difference between the energy of the actual molecule and that of an idealized molecule obtained by the following imaginary process: the rotation of the nuclei is gradually stopped without placing any new constraint on the vibration of the nuclei or on the electron motions, in such a way as might be realized by gradually (i.e. adiabatically) coupling an infinite moment of inertia to the axis of rotation of the molecule. In Eqs. (2c)–(4c), B_v and all the coefficients of powers of $(J+\frac{1}{2})^2$ then go to zero.

(2) The energy E_v is the difference between the energy of a molecule idealized just to the extent of making $E_r=0$ and the energy of a further idealized molecule obtained by the following imaginary process: the vibration of the nuclei is gradually stopped without placing any new constraint on the electron motions, in a way such as might be realized by leaving the charges of the nuclei unchanged but gradually increasing the masses until they are infinite. In Eqs. (2b)–(4b), ω_e and all the coefficients of powers of $(v+\frac{1}{2})$ then go to zero.

(3) The energy E_e is the total internal energy of a molecule in a definite electronic state with the nuclei stationary (this condition may be realized in imagination by making the masses infinite) at their equilibrium distance (r_e) apart. E_e consists of (a) kinetic energy of the electrons, plus (b) their potential energy with respect to the nuclei and to one another, plus (c) the mutual potential energy of repulsion of the two nuclei. As was mentioned above, $E_e \equiv U(r_e)$.

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with the meaning E_r/hc, and this usage is therefore recommended here (cf. Eq. (5)). The use of T for E/hc (or for $-E/hc$, measured from an arbitrary zero of energy at ionization) has been frequent in the field of line spectra. The use of G for E_v/hc (cf. Eq. (5) and ref. 38) was suggested by Birge and recommended in the National Research Council Report on Molecular Spectra, but this recommendation has not been widely followed.

Rotational term differences. In the analysis of band spectra, it is customary to use such designations as $\Delta F(J)$, $\Delta_1 F(J)$, $\Delta_2 F(J)$ for the difference between two rotational terms differing only in the value of J. [Formerly Δf and ΔF were often used to distinguish these term intervals respectively for the upper and lower of the two electron levels involved, but it is recommended that this distinction be made only by the use of (′) and (″), as in $\Delta F'$, $\Delta F''$].

It is recommended that in designating rotational term intervals, the forms which are defined in the following equations be used:[31,32]

$$\Delta_1 F(J + \tfrac{1}{2}) = F(J + 1) - F(J) \tag{6}$$

$$\Delta_2 F(J) = F(J + 1) - F(J - 1). \tag{7}$$

Examples,

$$\Delta_1 F(3\tfrac{1}{2}) = F(4) - F(3); \quad \Delta_2 F(4) = F(5) - F(3).$$

In all states with $\Lambda > 0$ there are, for a given value of Σ and of J in case a, or of K and of J in case b, two rotational levels (cf. Fig. 2). (These are usually very close together, but separate widely on approach to case d). This doubling may be called Λ-*type doubling* because it occurs if, and only if, $\Lambda > 0$. [It was formerly, but less correctly, called "σ-type doubling," where "σ" is a former designation for our present Ω.[33]] It is suggested that, in each

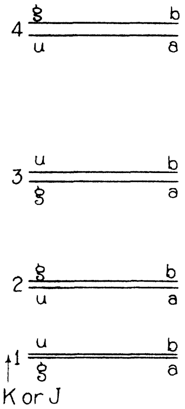

Fig. 2. Λ-type doublets for the case $S = 0$, $\Lambda = 1$. The order shown for the g and u levels represents only one of two possibilities; the case in which $1(g)$ lies above $1(u)$, $2(u)$ above $2(g)$, and so on, is the other (g and u respectively stand for even and odd[19a]). There is also no fixed rule as to the relative position of a and b levels; nor is there any fixed rule for correlating the a, b, and the g, u descriptions (cf. references 35, 36, 19a).

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[31] $\Delta_1 F(J+\frac{1}{2})$ and $\Delta_2 F(J)$ may be read as "delta one F $J+\frac{1}{2}$" and "delta two F J."

[32] $\Delta_1 F(J+\frac{1}{2})$ is commonly denoted by $\Delta_1 F(J)$, but the use of the symbol $\Delta_1 F(J+\frac{1}{2})$ as in Eq. (6) seems preferable. In practise, $\Delta_1 F(J+\frac{1}{2})$ is much less important then $\Delta_2 F(J)$, since $\Delta_1 F(J+\frac{1}{2})$ cannot be directly and exactly evaluated from the analysis of a spectrum; instead one usually obtains $F_a(J+1) - F_b(J)$, or $F_b(J+1) - F_a(J)$.

[33] The name "σ-type-doubling" was given by the writer before Hund's development of the theory of molecular electronic states, and was based on the idea that this type of doubling occurs whenever $\sigma > 0$ [in the present symbols, whenever $\Omega > 0$]. Later Hund showed that this doubling is to be expected, not whenever $\Omega > 0$ but whenever $\Lambda > 0$. *Usually* $\Lambda > 0$ and $\Omega > 0$

rotational doublet of this kind, the component levels be distinguished as a and b sublevels,[34] and that the term values be distinguished by corresponding subscripts, as, $T_a^{(v)}(J)$, $T_b^{(v)}(J)$, $F_a(J)$, $F_b(J)$.[16a,35,36] For rotational term differences, we have then $\Delta_2 F_a(J)$, $\Delta_2 F_b(J)$, $\cdots$ etc.

In case b, it is necessary to provide a means of indicating both K and J. The writer[36a] suggested the use of the symbols F_1, F_2; $\Delta_1 F_1$, $\Delta_1 F_2$; $\Delta_2 F_1$, $\Delta_2 F_2$ for case b with $S=\frac{1}{2}$, where F_1 refers to the terms with $J\text{–}K=+\frac{1}{2}$ and F_2 to $J-K=-\frac{1}{2}$. For $S=1$, the suggested symbols were F_1, F_2, F_3, for $J-K=+1$, 0, -1 respectively. These suggestions are now renewed,[36b] with the added suggestion that this use of numerical subscripts be applied both to the rotational terms F and to the complete terms T; when $\Lambda>0$, a and b subscripts are needed in addition to the numerical subscripts. Examples, $T_1^{(v)}(J)$; $T_{2a}^{(v)}(J)$; $F_{2b}(J)$; $\Delta_2 F_1(J)$; $\Delta_2 F_{1a}(J)$; $\Delta_2 F_{2b}(J)$; $\Delta_2 F_{2a}(J)$, etc.; specifically, $\Delta_2 F_{1a}(5\frac{1}{2})$ would mean $F_{1a}(6\frac{1}{2})-F_{1a}(4\frac{1}{2})$, with the K values 6 and 4. Sometimes when K is the important rotational quantum number, J is lacking in significance (case b', cf. Section II above). In such a case, one naturally will use such forms as $\Delta_2 F(K)$, $\Delta_2 F_a(K)$. Also when $S=0$, so that $J\equiv K$, one *may* use K instead of J as the argument of a ΔF expression.

Vibrational term differences. It is suggested that in designating vibrational term differences, the forms which are defined in the following equations be used:[37]

$$\Delta G(v+\tfrac{1}{2}) = G(v+1) - G(v) \tag{6}$$

$$\Delta^2 G(v)\left[\equiv \Delta G(v+\tfrac{1}{2}) - \Delta G(v-\tfrac{1}{2})\right] = G(v+1) - 2G(v) + G(v-1). \tag{7}$$

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go hand in hand. A familiar exception is $^3\Pi_0(\Lambda=1, \Omega=0)$. Experimentally this shows Λ-type doubling as predicted by Hund.

[34] The use of the designations A and B was suggested by the present writer (Phys. Rev., **30**, 791, 1928). Some people have followed this suggestion, others have substituted a and b. The difference is not essential, but a and b seem to be preferred by the majority. (These designations have nothing to do with Hund's cases a and b).

[35] The designations a and b are essentially temporary empirical labels, and have no *definite* relation to any designations of theoretical significance (but cf. ref. 36). For two formal schemes for choosing which levels to call a and which to call b, cf. (1) R. S. Mulliken, Phys. Rev. **28**, 1205 (1926) and (2) R. S. Mulliken, Phys. Rev. **30**, 791 (1927). Some writers follow the first scheme, more the second. Both schemes lead to the same use of the labels a and b in the case of Π states, but give opposite labellings in the cases of Σ and of Δ states.

[36] The division into a and b levels is related to the theoretical division (cf. Ref. 19a and Wigner and Witmer, l.c. Ref. 17) of all molecular terms into even or positive and odd or negative terms. In the case of Π states, if *either* of the methods of labelling mentioned in ref. 36 is followed, the result is *usually* that in the b set of sub-levels, the even-numbered levels are even and the odd-numbered are odd; in the a set of sub-levels, the relations are always the reverse of those in the b set. The nature of the correlation between a and b and even and odd levels is illustrated in Fig. 2. For the case of Σ levels, cf. reference 18. In the case of Δ, Φ, $\cdots$ levels, the relations are of the same type as in Π levels.

[36a] Cf. R. S. Mulliken, Phys. Rev. **30**, 788 (1927).

[36b] A more logical method would be to use the values of $J-K$ as subscripts, as in $F_{+\frac{1}{2}}(J)$, $F_{-\frac{1}{2}a}(J)$, $\Delta_2 F_{+\frac{1}{2}}(J)$, $Q_{-\frac{1}{2}-\frac{1}{2}}(J)$, instead of $F_1(J)$, $F_{2a}(J)$, $\Delta_2 F_1(J)$, $Q_{12}(J)$. But since the present notation is simple and reasonably satisfactory, it does not seem wise in this report definitely to suggest a change.

[37] $\Delta G(v+\frac{1}{2})$ and $\Delta^2 G(v)$ may be respectively read as "delta $Gv+\frac{1}{2}$" and "delta second Gv."

Examples, $\Delta G(3\frac{1}{2})=G(4)-G(3)$; $\Delta^2 G(4)=\Delta G(4\frac{1}{2})-\Delta G(3\frac{1}{2})=G(5)-2G(4)+G(3)$. It will be seen that the argument of ΔG is always a half-integer midway between the v values (always integers) of two energy levels, while the argument of $\Delta^2 G$ is always an integer. [$\Delta G(v+\frac{1}{2})$ as here used is synonymous with Birge's $\Delta G_{v+\frac{1}{2}}$ and with $\omega_{v+\frac{1}{2}}$ as introduced by Birge and Sponer.[38]]

Band and system origins. In describing a band spectrum, it is convenient to consider the frequency of each line as a sum of three parts, just as it is convenient to consider the energy and the term-value each as a sum of three parts (cf. Eqs. (1), (5)). Thus for the wave number ν we may write[39]

$$\nu = T' - T'' = (T_e' - T_e'') + (G' - G'') + (F' - F'') = \nu_e + \nu_v + \nu_r. \quad (8)$$

The concepts of the "origin" of a band and of a band system are frequently used in theoretical discussions. These can be unambiguously defined as follows:[39]

$$\text{System-origin: } \nu = \nu_e$$

$$\text{Band-origin: } \nu = \nu_e + \nu_v.$$

These definitions do not in general correspond to wave-number positions which are of importance in the analysis of band spectra, except in the study of the isotope effect. Band and system origins are discussed here only in order to remove possible misconceptions as to their meaning.

In *simple types* of bands, an equation for the band lines can often be given in the form

$$\nu = \nu_0 + aM + bM^2 + \cdots, \quad (9)$$

where M is a parameter which takes on positive and negative integral or half-integral values, related to values of K'' or J''. The line given by $\nu=\nu_0$, and often other lines, are ordinarily missing. In the simplest cases, ν_0 is approximately the same as $\nu_e+\nu_v$, but the agreement is never exact if we use accurate expressions for E_e, E_v, and E_r; and the difference between ν_0 and $\nu_e+\nu_v$ varies from one type of band to another. The term "band-origin" is often loosely applied to ν_0, but it is evident that this usage is inaccurate and tends to produce confusion.

In a system of bands, the band origins can be expressed by the equation

$$\nu_e + \nu_v = \nu_e + \omega_e'(v' + \tfrac{1}{2}) - \omega_e''(v'' + \tfrac{1}{2})$$
$$- x_e'\omega_e'(v' + \tfrac{1}{2})^2 + x_e''\omega_e''(v'' + \tfrac{1}{2})^2 + \cdots. \quad (10)$$

The origin of the 0, 0 band (obtained by putting $v'=0$, $v''=0$ in Eq. 10) obviously does not coincide with the origin of the band system ($\nu=\nu_e$). If

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[38] For the original proposal to use ΔG, cf. the National Research Council Report on Molecular Spectra, p. 123, Eq. (76). (In Eq. (76) the old symbol n appears instead of v.) In regard to $\omega_{v+\frac{1}{2}}$ cf. R. T. Birge and H. Sponer, Phys. Rev. **28**, 259, (1926).

[39] Where ν_v, ν_r are used here, other designations such as ν_n, ν_m are frequently used. No definite recommendation of ν_e, ν_v, and ν_r is intended here, although they are preferred by the present writer. It is pretty obvious, however, that ν_n and ν_m should be dropped, since their subscripts are the now discarded symbols n and m formerly used for the vibrational and rotational quantum numbers.

the old quantum theory formula for E_v (cf. Eq. (2)) were correct, the system-origin *would* coincide with the origin of the 0, 0 band. In existing tables of band spectrum data, based on the old quantum theory formulation, the origin, or even the ν_0 position, of the 0, 0 band is in fact commonly referred to as the system-origin.[39]

Designations for band systems and bands. For designating a transition between two electronic states, it is suggested that the following forms be used: $^2\Pi \rightarrow {}^2\Sigma$ for emission bands (to be read "$^2\Pi$ to $^2\Sigma$"); $^2\Pi \leftarrow {}^2\Sigma$ for absorption bands (this might be read "$^2\Pi$ from $^2\Sigma$"); and simply $^2\Pi$, $^2\Sigma$ in general discussions. It is recommended that the equivalent form $^2\Sigma - {}^2\Pi$, which is analogous to atomic symbolism such as $1s-2p$, be abandoned.[40] In the suggested symbols, the *first mentioned* (here $^2\Pi$) always refers to the state of higher energy.

In indicating the two vibrational levels concerned in the production of a particular band, one speaks of the (0, 3) band, the (5, 2) band, and so on, where the first number refers to v', the second to v''. Usually the parentheses can safely be dropped, so that one can write "the 0, 3 band," and so on.

Designations for band-lines. The lines of a band can always be divided into one or more series ("branches"). For all the lines in one branch, $J'-J''$ (also $K'-K''$ in case *b*) has a constant value. *It is recommended* that the symbols O, P, Q, R, S be used, in a way now to be described, to denote various types of branches. In *case a*, we define

$$\begin{aligned}
O(J) &= T'(J-2) - T''(J) = \nu_e+\nu_v+F'(J-2) - F''(J)\\
P(J) &= T'(J-1) - T''(J) = \nu_e+\nu_v+F'(J-1) - F''(J)\\
Q(J) &= T'(J) \qquad - T''(J) = \nu_e+\nu_v+F'(J) \qquad - F''(J)\\
R(J) &= T'(J+1) - T''(J) = \nu_e+\nu_v+F'(J+1) - F''(J)\\
S(J) &= T'(J+2) - T''(J) = \nu_e+\nu_v+F'(J+2) - F''(J)
\end{aligned}$$

In these symbols, the usual arbitrary convention has been adopted of *using the value of J''*, rather than that of J' or of $\frac{1}{2}(J'+J'')$, *as the argument*, but at the same time *substituting the symbol J* for the symbol J'' for the sake of brevity. *It is recommended* that, to avoid confusion, the convention of using the value of J'' as argument be uniformly followed.

Branches $O(J)$ and $S(J)$ ordinarily exist only in Raman spectra, and there only in the form

$$\nu = \nu_{exc} \mp [O(J) \text{ or } S(J)].$$

Here ν_{exc} is the wave number of the exciting line; in $O(J)$ or $S(J)$, ν_e is zero in the cases usually investigated (vibration-rotation Raman bands), or ν_e and ν_v are both zero and at the same time we have only $S(J)$, not $O(J)$ (pure rotation Raman bands).

When, in *case b*, the fine structure corresponding to different values of $J-K$ is unresolved (case b', cf. Section III), or narrow, one will naturally

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[40] The form $^2\Sigma - {}^2\Pi$ is really sensible only in case each term is a member of a series converging to a known limit from which the term can be *measured downwards*. Except in H_2 and He_2 such series are not known for molecular terms, and the use of the corresponding notation has no point. Even in atomic spectra, its usefulness is limited to the simplest types of series spectra.

define and use $O(K), P(K), \cdots$, in analogy to $O(J)$, $P(J)$, $\cdots$, of case *a*. For example, in a $^2\Sigma$, $^2\Sigma$ transition, one has a branch $P(K)$ and a branch $R(K)$, each line of each branch being a usually narrow, often unresolved, doublet.[41] Also when $S=0$, so that $J=K$, one may use K instead of J as argument.

In cases where both ΔK and ΔJ are important, it is necessary to designate both. For this purpose symbols such as $Q_{21}(J)$, $R_{12}(J)$, etc. are suggested, in which J'' (*written as* J) is used as argument in the usual manner, and in which the numerical subscripts indicate values of $J-K$. It was suggested above that the rotational term designations F_1, F_2, F_3, $\cdots$, be used in case *b* for $J=K+S$, $K+S-1, \cdots, |K-S|$. Similarly,[35] one may speak of branches $Q_{21}(J)$, $R_{11}(J)$, $Q_{22}(J)$, $Q_{12}(J)$, etc., where the first numerical subscript refers to the upper energy level, the second to the lower. (Symbols such as $R_{11}(J)$ and $Q_{22}(J)$ can ordinarily be abbreviated to $R_1(J)$ and $Q_2(J)$.) For example, $Q_{21}(5\frac{1}{2})$ means $\nu_e+\nu_v+F_2'(5\frac{1}{2})-F_1''(5\frac{1}{2})$, or, more briefly expressed, $T_2'(5\frac{1}{2})-T_1''(5\frac{1}{2})$; here $K'=6$, $J'=5\frac{1}{2}$, $K''=5$, $J''=5\frac{1}{2}$, so that $K'-K''=+1$, while $J'-J''=0$. This notation is incomplete, however, until designations are added to indicate the *a* or *b* character of the rotational levels involved. When this is included, we have symbols such as $Q_{2a1a}(5\frac{1}{2})$, $Q_{2b1b}(5\frac{1}{2})$, $R_{1a1b}(J)$, $R_{1b1a}(J)$, $Q_{2b1b}(J)$, and $Q_{2a2a}(4\frac{1}{2})$ or more briefly $Q_{2}(4\frac{1}{2})$. If Λ' or Λ'' is zero, the *a* or *b* subscripts can be omitted.[36] The notation just suggested can be made more explicit by the addition of a superscript symbol to indicate $K'-K''$; examples, $^RQ_{2a1a}(5\frac{1}{2})$, $^RR_{1a1b}(J)$. The added superscript is, however, not necessary, since the value of $K'-K''$ is already implied in the remainder of the symbol. For a more detailed discussion of this notation, references 35 and 36 may be consulted.

In the analysis of band spectra, temporary designations for band lines are sometimes needed before the true J or K values involved are known. *It is recommended* that in such cases the lines and branches be designated and numbered in some way that will not be confused with approved theoretically significant designations. For example, one might use $X(m)$, $Y(m)$, $Z(m)$, etc.; or if ΔJ or ΔK is known, but the correct numbering is uncertain, $P(m)$, $R(m)$, etc.; or $P_\alpha(m)$, $P_\beta(m)$, $R_\gamma(m)$, $R_\delta(m)$, etc. The parameter m could be given values 1, 2, 3, $\cdots$.

CONCLUSION

In Table I some of the most important changes recommended or suggested here are summarized.

TABLE I. *Some new designations and some of their older equivalents.*

New	Old	New	Old
v	n	λ	i_{l_T}, σ_{l_T}, σ_{k_T}
J	j, m, etc.	σ, π, δ, $\cdots$	s, p, d, $\cdots$
M	(magnetic quantum number)	$\left\{\begin{array}{l}2p\sigma,\ 3s\sigma,\\ 3p\pi,\ 3d\sigma,\ \text{etc.}\end{array}\right.$	$2s^p$, $3s^s$ $3p^p$, $4s^d$, etc.
Λ	i_l, σ_k, σ_l	T; T_e; G	E/hc; E_e/hc; E_v/hc
Σ	i_s, σ_s, X	Λ-type doubling	σ-type doubling
Ω	i, σ	$^2\Pi\rightarrow{}^2\Sigma$, or $^2\Pi$, $^2\Sigma$; etc.	$^2\Sigma-{}^2\Pi$, etc.
K	p_l, j_k	Σ^+, Σ^-	Σ, Σ'
Σ, Π, Δ, $\cdots$,	S, P, D, $\cdots$	Σ_g, Σ_u, Π_u, Π_g, etc.	

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[41] Strictly, each line except the first is a triplet (cf. R. S. Mulliken, Phys. Rev. **30**, 138, **1927**).

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