THE INTERPRETATION OF BAND SPECTRA. PART IIc. EMPIRICAL BAND TYPES

BY ROBERT S. MULLIKEN*
UNIVERSITY OF CHICAGO

TABLE OF CONTENTS

---

* A large part of this article was written during the tenure of a John Simon Guggenheim Memorial Fellowship.

A. Symbols and Notation[51]

IN PART II*c* the symbols T^e or T_e, G, F, $\nu_e,\nu_v,\nu_r,\nu_0,\Delta G(v+\frac{1}{2})$ are used instead of $F^{el},F^v,F^r,\nu^{el},\nu^v,\nu^r,\nu^0$, and $\Delta F^v(v_1,v_2)$ of Parts I, II*a*, II*b*. In place of the more or less inaccurately defined subscripts *a* and *b* of Part II*b*, more clearly defined subscripts *c* and *d* are introduced (cf. section *C*3) for differentiating the members of a Λ-type doublet, and *e* and *f* for the Ω-type doublets of case *c* (cf. section *H*1). In this section and hereafter we shall speak of "regular" and inverted multiplet states ($A > 0$ and $A < 0$) instead of "normal" and inverted states. Other symbols used here are the same as before, but certain additional symbols and expressions have been introduced, as follows:

Positive and negative (+and−) rotational levels, cf. section *C*1
Σ^+ and Σ^- electron states, cf. section *C*2
Q branch = series of band-lines having $J' = J''$
$\Delta J = J' - J''$; $\Delta K = K' - K''$
$\kappa,\delta,\epsilon,\mu,\eta$ = small coefficients (cf. Eqs. 56, 63)
B^x,D^x (cf. Eq. 57)
Sub-bands and sub-systems, cf. section *G*1

---

[51] For a general discussion of band spectrum notation cf. Report on Notation, R. S. Mulliken, Phys. Rev. **36**, 611 (1930).

Even and odd (g and u) electron states (of molecules composed of two atoms of the same element): cf. section $K1$

Symmetrical (Sy) and antisymmetrical (An) wave-functions ψ: cf. section $K2$

Symmetrical (s) and antisymmetrical (a) wave-function factors ψ_{nu} of the nuclear angular momentum: cf. section $K2$.

B. PRELIMINARY REMARKS

Before beginning the discussion of band types, which is the object of Part II*c*, it is necessary to describe certain properties of molecular energy levels which have not yet been considered. This is done in Section *C*. The terminology used in describing Λ-type doubling is also revised (Section *C*3). Later on (Section *K*) it will be necessary to go into certain additional properties of molecules composed of two atoms of the same element, before discussing the spectra of such molecules. Sections *H*1 and *H*3 also contain new material on the nature of case *c* and its relations to cases *a* and *b*.

A good brief treatment of the structure of electronic bands has recently appeared in Ruark and Urey's "Atoms, Molecules, and Quanta," and a more complete one in R. Ruedy's "Bandenspektren auf experimenteller Grundlage."[52, 59] For this reason it has seemed best to make the account here given more detailed than was at first intended. For those not interested in details of band structure, a study of the figures is suggested as the best way of getting a general idea of the various types of bands and their relation to energy levels. For such readers Sections *C*1, *C*2, and *K* should also be of interest.

It was originally the writer's intention to prepare as a portion of Part II*c* a discussion of the evaluation of molecular constants by the analysis of band spectra.[52] This, however, will be postponed until after Part III is finished.

C. POSITIVE AND NEGATIVE ROTATIONAL LEVELS. Σ^+ AND Σ^- ELECTRON STATES. REVISED NOMENCLATURE FOR USE IN Λ-TYPE DOUBLING

1. *Positive and negative rotational terms.* Before entering on the discussion of band types, it is necessary to describe certain properties of the energy levels of diatomic molecules which have not yet been considered. In the absence of disturbing external fields, all molecular energy levels or terms can be divided rigorously into two classes, which Kronig has called even and odd, and Wigner and Witmer have called positive and negative.[53] We shall use here the latter terminology, in order to avoid possible confusion with Hund's earlier use of the words even and odd in describing the *electron states* of molecules composed of two atoms of the same element (cf. section *K*1 below).

---

[52] Cf. R. T. Birge, National Research Council Bulletin on Molecular Spectra (1926), for earlier detailed accounts.

[53] R. de L. Kronig, Zeits. f. Physik **50**, 347–362 (1928). E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859–886 (1928). For definitions of positive and negative terms cf. Wigner and Witmer, *l. c.*, p. 865, second paragraph, and p. 867, first footnote; Kronig. *l.c.*, p. 351. Positive and negative molecular terms are defined in the same manner as the even and odd (Wigner's positive and negative) terms of atoms.

The difference between positive and negative rotational levels can be explained only in terms of the quantum mechanics. The complete Schrödinger wave-function ψ for any stationary state of the molecule, expressed as a function of the coordinates $x_a y_a z_a$, $x_b y_b z_b$, $x_1 y_1 z_1 \cdots$, $x_n y_n z_n$ and spins s of the two nuclei (a and b) and n electrons, always has the property either that $\psi(-x_a, \cdots, -z_n, \text{spins}) = \psi(x_a, \cdots, z_n, \text{spins})$, or else that $\psi(-x_a, \cdots, -z_n, \text{spins}) = -\psi(x_a, \cdots, z_n, \text{spins})$. In the former case we speak of positive, in the latter of negative levels.

2. *Σ^+ and Σ^- electron states.* As has been noted in Parts II*a*, II*b*, [54, 55] the electron state of any molecule with normal coupling (case *a* or *b*) is characterized by quantum numbers S and Λ. When $\Lambda > 0$, we have "Λ-type doubling" so that, in addition to the spin multiplicity which is present if $S > 0$, each rotational level is a doublet composed of an "*a*" and a "*b*" sub-level.[54,55] In each such doublet, one component is a positive, the other a negative level. The nature of the relation between the *a*, *b* (now revised to *c*, *d*, cf. section *C*2) and the +, − designations can be seen from Fig. 17.

When $\Lambda = 0$(Σ states), there is no Λ-type doubling in the rotational levels. Instead we find that there are two kinds of Σ states. The most usual are the Σ^+ states, which have positive rotational levels for even values of K, negative levels for odd K values. But there are also Σ^- states, which have negative levels for even K and positive levels for odd K. These descriptions of Σ^+ and Σ^- states hold for ${}^2\Sigma, {}^3\Sigma, \cdots$, states as well as for ${}^1\Sigma$ states (cf. Fig. 17 for ${}^1\Sigma^+$ and ${}^1\Sigma^-$ and Fig. 24 for ${}^2\Sigma$ states). The real reasons why the two types Σ^+ and Σ^- are possible cannot conveniently be stated here, but will be given in Part III. Of Σ^- states, only a few are as yet definitely known to exist, namely one excited ${}^2\Sigma^-$ state in CH, and six or eight ${}^3\Sigma^-$ states. Of the latter two are the normal states of NH and PH,[104a] one is the normal state of O_2, one is the excited state of the Schumann-Runge bands of O_2, while S_2 and probably also SO each have two ${}^3\Sigma^-$ states analogous to those of O_2.[55a] A probable ${}^1\Sigma^-$ state is also known in O_2 (cf. end of section *D*1).

3. *Revised nomenclature for use in Λ-type doubling.* In Part II*b* the two members of a Λ-type doublet were referred to as *a* and *b* sublevels. The designations *a* and *b* hitherto defined have been little more than arbitrary empirical labels. Two formal schemes for choosing which levels to call *a* and which to call *b* have been proposed by the writer,[56] but neither of these makes it possible to define *a* and *b* rotational levels unambiguously in terms of theoretically significant quantities such as J and K values and + or − char-

---

[54] Parts I, II*a*, II*b*, R. S. Mulliken, Reviews of Modern Physics, **2**, 60–115 (1930).

[55] Additions and Corrections for Parts I, II*a*, II*b*, R. S. Mulliken, Reviews of Modern Physics, **2**, 506–8 (1930).

[55a] For a discussion of the electron states of O_2, cf. R. S. Mulliken, Phys. Rev., 1931. Interpretation of S_2 bands, S. M. Naudé and A. Christy, Phys. Rev. **36**, 1801 (1930). SO bands, E.V. Martin and F. A. Jenkins, Bull. Am. Phys. Soc. **5**, No. 6, p. 7 (Los Angeles Meeting, 1930).

[56] Scheme (1): R. S. Mulliken, Phys. Rev. **28**, 1205 (1926). Scheme (2): R. S. Mulliken, Phys. Rev. **30**, 791 (1927). Most writers follow the second scheme. 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 case of Σ as well as in that of Δ states.

acter. In the interest of clarity in the following exposition, it seems important to redefine *a* and *b* levels so that they will have a definite theoretical meaning, and this is done in a later paragraph.

One might of course think that it would be sufficient to classify levels according to their + or − character, but experience shows that an additional and different sort of classification essentially of the *a*, *b* kind is too useful to be dropped. The relationship between the two kinds of classification can be seen from some of the diagrams of Fig. 17. The *a* levels of any electronic state form one continuous set, the *b* levels another, while + (also −) levels belong alternately to the *a* and to the *b* set.

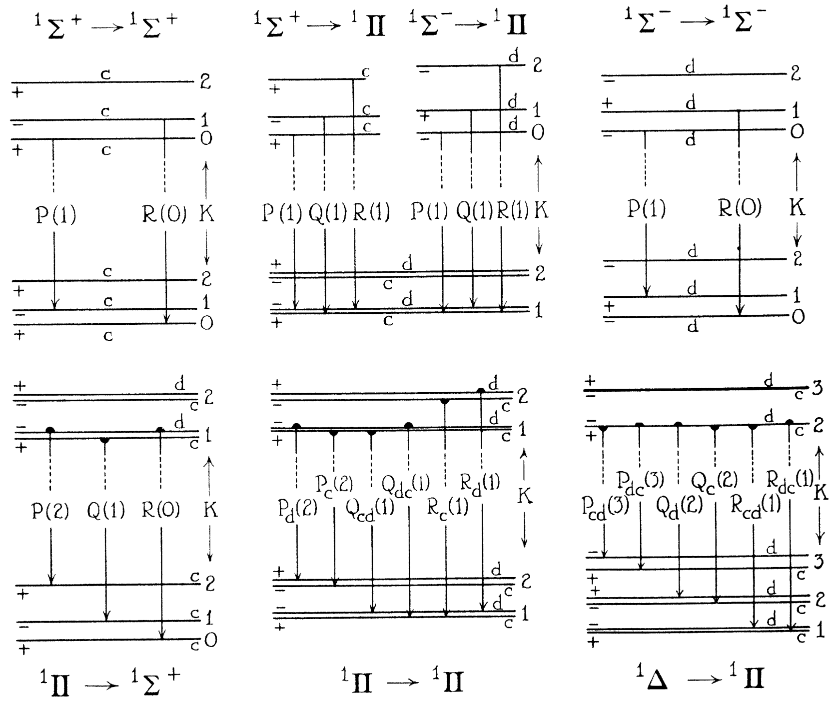


Fig. 17. Rotational energy levels and transitions for most of the important singlet band types. Only the lowest few rotational levels are shown for each electron state. The widths of the Λ-type doublets for the $^1\Pi$ states are drawn proportional to $K(K+1)$, while the $^1\Delta$ doublets are shown with negligible separations (cf. section *F*2 and Ref. 71). The doublet widths in the $^1\Pi$ states are, however, all exaggerated in order to make them clearly visible. The only rotational transitions shown are those corresponding to the lowest-numbered possible line in each branch. These are, however, sufficient to illustrate the selection rules and the nomenclature. (Cf. also Fig. 2, where a larger number of band lines is shown, for the $^1\Sigma$, $^1\Sigma$ type of band.) The figure shows the meaning of the symbols Σ^+, Σ^-, and of *c* and *d* levels, in terms of K values ($K \equiv J$ here) and positive or negative (+ or −) character of rotational levels (cf. text, section C).

The *order* of the + and − (or *c* and *d*) levels in Λ-type doublets, for a definite value of Λ and of K, is not always the same as that shown in Fig. 17. For example, Fig. 17 shows the − level above the + level for $K=1$ in $^1\Pi$ states, whereas in practice the reverse arrangement is also possible (cf. Part II*b*, Ref. 39). The arrangements shown in Fig. 17 are, however, those which appear to be most usual in practice.

In the first place, we shall substitute the letters *c* and *d* for the redefined *a* and *b*. (These particular letters were chosen after careful consideration as being about the least objectionable designations available.) In this review we shall hereafter always use *c* and *d*. It is suggested that these designations be adopted also in empirical spectroscopy whenever they can be assigned with a reasonable degree of certainty. But when this cannot be done, it is suggested that *a* and *b* be used as temporary designations, just as hitherto. In most but not in all of the cases where *c* and *d* can now be assigned to empirically known levels it will be found that they are respectively equivalent to the old *a* and *b*.

For *singlet and case b* states, we define *c* and *d* levels as follows. We designate every series of levels *whose lowest K value* $(0,1,2,\cdots$, for $\Sigma, \Pi, \Delta, \cdots$, states) corresponds to a $+$*level* or group of levels as a *c series*, every series whose *lowest K value* corresponds to a $-$*level* or levels as a *d series* (cf. Figs. 17,25,26 for examples). In every *c* series, the levels alternate $+-+-\cdots$, in every *d* series they alternate $-+-+\cdots$. This definition causes all the rotational levels of a Σ^+ state to be classed as *c* levels, those of a Σ^- state as *d* levels, so that we might speak of Σ^c and Σ^d instead of Σ^+ and Σ^- states. In Π states one may often conveniently regard the *c* and *d* sets of levels as respectively associated with a Π^c and a Π^d electronic substate, although strictly this is not justified, since the division into *c* and *d* levels comes about only as a result of the rotation. Analogous statements apply to Δ and other levels. The concept of *c* and *d* electronic substates has already been utilized for the spectra of He_2, where the symbols $\Pi_a, \Pi_b, \Delta_a, \Delta_b$, (also Σ_a and Σ_b) are much used.[57]

The definitions of *c* and *d* levels in case *a* can best be made by considering the adiabatic correlation of cases *a* and *b*. This is the same procedure that was used (cf. Part II*b*, pp. 112–13) to define $F_1, F_2, \cdots$, levels in case *a*, and has the same advantage, namely that it provides a consistent and reasonably convenient notation for all intermediate cases between *a* and *b*. The results[58] are summarized in Table V (cf. Figs. 22 and 28 for examples).

---

[57] The known Σ levels of He_2 are all Σ^+ levels, hence could all be called Σ^c. For the $p\Pi$ and $d\Delta$ levels, *a* and *b* as now used for the He_2 levels are respectively equivalent to *c* and *d*. For the $d\Pi$ levels, *a* and *b* as used by Dieke respectively correspond to *d* and *c*.

[58] The adiabatic correlation of case *a* with case *b* $^2\Pi$ states can be followed by means of Fig. 16 of Part II*b*. Let us assume that the dark and light circles in Fig. 16 respectively correspond to positive and negative levels. [Either this or the reverse is necessarily true, but this correlation (dark = positive) corresponds to what is the usual energy order in practise.] Then for $K=1, 3, 5, \cdots$ in case *b* the positive (dark) circles are *c* levels, the negative (light) circles are *d* levels, while for $K=2, 4, \cdots$ the negative circles are *c*, the positive *d*. Now let us follow through the *c* and *d* levels to inverted case *a*. We then find that $^2\Pi_{\frac{1}{2}}$ begins $(J=\frac{1}{2})$ with a positive *c* and a negative *d* level, and that $^2\Pi_{1\frac{1}{2}}$ also begins $(J=1\frac{1}{2})$ with a positive *c* and a negative *d* level. Thus the definitions of *c* and *d* levels here are very similar to those in case *b*. For *regular* $^2\Pi$ states, the definitions of *c* and *d* levels prove, however, to be reversed. We find that $^2\Pi_{1\frac{1}{2}}$ begins $(J=1\frac{1}{2})$ with a negative *c* and a positive *d* level. *I.e.*, the *c* levels are $-+-+\cdots$, the *d* levels $+-+-\cdots$ [The reason for this is simply that the lowest level $J=1\frac{1}{2}$ of $^2\Pi_{1\frac{1}{2}}$ is derived from the second level $K=2$ of case *b* instead of from $K=1$; for inverted $^2\Pi$, however, the lowest levels of both $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ were derived from $K=1$ of case *b*.] In $^2\Pi_{\frac{1}{2}}$

In *case c* there are double rotational levels whenever $\Omega > 0$. The two series of levels in this case will be distinguished here as *e* and *f* levels (cf. section *H*1 and Table V).

TABLE V. *Definitions of c and d rotational levels for various kinds of electronic states*

Kind of State	Character of lowest rotational level*	Series* Designation
All Σ^+ states	+	*c*
All Σ^- states	−	*d*
All other singlet and case *b* states	+ −	*c* *d*
Regular case *a* doublet states ($^2\Pi_{\frac{1}{2}}$, $^2\Pi_{1\frac{1}{2}}$, $^2\Delta_{1\frac{1}{2}}$, etc.)	− +	*c* *d*
Inverted case *a* doublet states	+ −	*c* *d*
Regular and inverted case *a* triplet states ($^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$, $^3\Delta_1$, etc.)	+ −	*c* *d*
Case *c* states	+ −	*e* *f*

* By the "lowest rotational level" is meant in singlet or case *b* states the level (*or group of levels*) of lowest *K* value, in case *a* states, the level of lowest *J* value. When the lowest level is +, succeeding members of the same series (cf. examples in Figs. 17, 24, 25) alternate in character (+ − + − · · ·); when it is −, they also alternate (− + − + · · ·).

In the text of Part II*b* (from p. 100 on), the letters *c* and *d* should be respectively substituted for *a* and *b* everywhere where *a* and *b* refer to Λ-type doublets. Also in Figs. 13 and 14, *a* and *b* should be replaced by *c* and *d*, except in the case of the $^1\Delta$ levels in Fig. 14, where they should be respectively replaced by *d* and *c*.

D. INTRODUCTION TO PART IIc

1. *Objects of Part IIc.* In Part II*b* we have considered[54,55] the possible types of electronic states of molecules, for various kinds of coupling of the electronic and nuclear angular momenta. In particular, energy formulas have been obtained for the various cases. In Part I we have considered[54] the band structure, including intensity relations, for the simple case of a transition between two $^1\Sigma$ states, and have seen how this structure varies with the temperature T and with the values of the coefficients B' and B''. We have also seen how the arrangement and intensity distribution of the bands in the band system are related to the values of B' and B'', hence to

---

we find that the first and second levels $J=\frac{1}{2}$ and $J=1\frac{1}{2}$ *both* have a positive *c* and a negative *d* level, which is contrary to our principle that *c* and *d* levels shall be alternately positive and negative. A little study shows that the level $J=\frac{1}{2}$ is anomalous, so that we may best assume for this one level that *c* changes to *d* and *d* to *c* in passing from case *b* to case *a*; an analogous assumption had to be made (cf. Ref. 49 of Part II*b*) in regard to the F_1 or F_2 character of this same level. The net result is then that for case *a* regular $^2\Pi_{\frac{1}{2}}$ we have − + − + · · · for the *c* levels and + − + − · · · for the *d* levels. Similar methods give similar results for case a $^2\Delta$ levels. Application of similar methods to case *a* $^3\Pi$ states shows that for regular as well as for inverted $^3\Pi$, the *c* levels are always + − + − · · · and the *d* levels − + − + · · · just as in case *b*.

the internal structure of individual bands. In Part II*c* we shall now consider how the structures of bands and the intensity relations within them depend on the nature of the initial and final electronic states, in other than $^1\Sigma,^1\Sigma$ transitions.

The object of Part II*c* is to explain and describe the types of bands found in practise. The type to which the bands of a new spectrum belong can then often be tentatively determined by comparison with these standard types. [As an aid to this, valuable and rather full descriptions of the structures of important bands of a number of molecules will be found compiled in R. Ruedy's recent book.][59] It should be pointed out, however, that in many cases it is necessary to resort to a rigorous analysis in order to determine the band-type. Such analysis is also necessary in order to determine from band spectra the positions of the molecular energy levels and the values of molecular constants. It is hoped in a later article to discuss methods of analysis.

No systematic discussion of intersystem combinations is given in Part II*c*, since very little is yet known about the band structures in such cases One rather well-known example is the atmospheric oxygen band-system, which is probably $^1\Sigma_u^- \leftarrow {}^3\Sigma_g^-$, but may be a quadrupole transition (cf. section *D*2) $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$.[60] The only other known band spectra now classified as intersystem transitions are the visible halogen bands[77] and certain systems in CO, e.g. the Cameron bands ($^3\Pi$, $^1\Sigma$).

2. *Selection rules for molecules.* The possible types of electronic transitions in molecules are limited by certain selection rules which will only be summarized here. The most important of these is $\Delta\Lambda = 0, \pm 1$, which holds whenever Λ is a good quantum number, as it is in the two most usual coupling cases (cases *a* and *b*). The rule $\Delta\Omega = 0, \pm 1$ also holds strictly whenever Ω is rigorously quantized (cases *a* and *c*). $\Delta\Sigma = 0$ holds strictly in case *a*, where Σ is rigorously quantized. In molecules composed of two atoms of the same element the important rule that "even" electron states combine only with "odd" states (cf. section *K*1) holds strictly.

Considering now the rotational levels, we always have $\Delta K = 0, \pm 1$ whenever K is rigorously quantized, as in cases *b*, *b'*, *d*, *d'*; and $\Delta J = 0, \pm 1$ whenever J is rigorously quantized, as is always true except when S is very loosely coupled to K in cases *b'* and *d'*. In cases *d*, *d'*, *e* we have $\Delta R = 0$ in electronic bands. In addition to the restrictions just given, the important rule that positive terms combine only with negative terms ($+ \rightleftarrows -$ only) holds strictly in all coupling cases. In external electric fields, however, this rule becomes less strict. Some OH band lines which violate the $+ \rightleftarrows -$ rule[61] have been explained as caused by such fields.

The above selection rules all refer to the dipole radiation. If we consider also the (usually vastly weaker) quadrupole radiation,[114] they do not hold.

---

[59] R. Ruedy, Bandenspektren auf experimenteller Grundlage, F. Vieweg, Braunschweig (1930). [For a correction, cf. last sentence in Ref. 89.] Cf. also Refs. 90, 91.

[60] Analysis and interpretation, R. S. Mulliken, Phys. Rev. **32**, 880–887 (1928), and Phys. Rev. 1931. Intensity relations, W. H. J. Childs, Nature, April 19, 1930, p. 599.

[61] Cf. R. S. Mulliken, Phys. Rev. **32**, 406 and 997 (1928). The "Q_{1A1B}" and "Q_{2A2B}" branches of Fig. 3 violate the $+ \rightleftarrows -$ rule.

A possible example of a quadrupole transition has been mentioned at the end of section *D*1. The foregoing dipole selection rules can be justified briefly as follows:

The rules $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0$ and $\Delta\Omega = 0, \pm 1$ which hold for the case of fixed nuclei (Part II*b*, p. 96 and Ref. 36), hold equally for case *a*, since in case *a* the rotation of the nuclei does not appreciably disturb Λ, Σ, and Ω. In case *b* $\Delta\Lambda = 0, \pm 1$ still holds, for the same reason, but Σ and Ω no longer exist on account of the rotation.

The rule $\Delta K = 0, \pm 1$ in molecules is precisely analogous to the rule $\Delta L = 0, \pm 1$ for atoms, and $\Delta J = 0, \pm 1$ in molecules to $\Delta J = 0, \pm 1$ in atoms. K and J in molecules refer to the (resultant electronic plus nuclear) orbital and to the total angular momentum just as L and J in atoms refer to the (resultant electronic) orbital and to the total angular momentum. The rule that positive molecular terms can combine only with negative terms is the exact analogue of the rule that even atomic terms can combine only with odd terms. (In this connection cf. Ref. 53, last sentence.) In regard to the selection rules for R, cf. section *F*3.

E. CASE *a* AND *c* AND SINGLET AND CASE *b′* BANDS: GENERAL RELATIONS

1. *Introduction.* It is convenient to begin the discussion of band-types by setting forth certain general relations which hold for frequencies and intensities whenever J and Ω exist as well-defined quantum numbers in both initial and final states of the molecule. This condition is fulfilled in all transitions involving *singlet* or *case a* or *case c* states, exclusive of case *d′* singlet states. Case *d′* singlet states, and cases intermediate between these and ordinary singlet states will, however, be treated in section *F*3.

Ordinary singlet states can be regarded as case *a* states having $\Sigma = S = 0$ and so $\Omega \equiv \Lambda$, and having $J \equiv K$. In discussing singlet states (exclusive of case *d′* states) in Parts I and II*b*, we have regarded them as case *b′* states and used the symbols Λ and K, but we can equally well treat them as case *a* states and use Ω and J. This we shall do in the present section. In later sections where we wish to emphasize their genetic relation to case *b* states we shall return, however, to Λ and K.

It should be noted that all the results of the present section, as well as of the next section (*F*), are directly applicable to case *b′* bands with $S > 0$, although here we *must* replace Ω and J of sections *E* and *F* by Λ and K.

2. *Equations for frequencies of band lines.* In order to get an expression for the frequency of any line in a band associated with a transition between two case *a* states, we take $\nu = T' - T''$ as in Eq. (7) of Part I. For T' and T'' we use expressions of the form given by Eq. (31) of Part II*b*. (For the case $S = 0$ these reduce to those given by Eq. 29). Letting[62]

---

[62] This expression for ν_0 applies only for the usual case $\Delta S = 0$. Since in this case $\Delta\Sigma = 0$ also holds, the quantity S_{perp} ($S_{perp}^2 = S^{*2}\Sigma^2$) is the same for the initial and final states. The quantity ν_e is equal to $T_0^{e\prime} - T_0^{e\prime\prime} + \Sigma(A'\Lambda' - A''\Lambda'')$. If $S = 0$, the term $\Sigma(A'\Lambda' - A''\Lambda'')$ drops out, as do also the S_{perp} terms.

$$\nu_0 = \nu_e + \nu_v - B'(\Omega'^2 - \overline{G^2}' - S^2{}_{perp}) + B''(\Omega''^2 - \overline{G^2}'' - S^2{}_{perp}),$$

and for simplicity writing B' and B'' in place of $B'_{v'}$ and $B''_{v''}$ and D' and D'' in place of $D'_{v'}$ and $D''_{v''}$, the result may be written (cf. Eq. 8 of Part I):

$$\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1) + \phi'(J') - \phi''(J'') + D'J'^2(J'+1)^2 - D''J''^2(J''+1)^2 + \cdots . \quad (49)$$

In the case of singlet states, Ω can be replaced by Λ, and J by K, if desired. For a transition between two case c states, Eq. (49) holds just as for case a states, although the constant ν_0 has a somewhat different meaning, which can be obtained by using T' and T'' expressions of the form of Eq. (68).

The possible frequencies given by Eq. (49) are limited by the selection rule $\Delta J = 0, \pm 1$. (By ΔJ is meant $J' - J''$.) For singlet states, ΔJ is identical with ΔK of the case b' viewpoint. When $\Delta J = 0$, we have a "zero" (Q) branch. When $\Delta J = +1$ or -1, we have respectively a positive (R) or a negative (P) branch (cf. Part I, p. 69). In addition to the rule $\Delta J = 0, \pm 1$, the rule that positive terms combine only with negative terms is important.[63] As a result of this rule, each branch consists of single lines if Λ' or Λ'' is zero, and of double lines if Λ' and Λ'' are both greater than zero.[64] Why this is true can be understood from Fig. 17.

For the R branch or branches, the following Eq. (50) is readily obtained by putting $J' = J'' + 1 = M$ in Eq. (49) and multiplying out. (Cf. Part I, Eqs. 8–11 and accompanying text.) The object of the substitution of M for $J'' + 1$ is to simplify the form of Eq. (50), and also to make this as nearly as possible like that of Eq. (51).

$$R_{ij}(M) = \nu_0 + (B' + B'')M + (B' - B'' + D' - D'')M^2 + \phi_i'(M) - \phi_j''(M-1) + 2(D' + D'')M^3 + (D' - D'')M^4 + \cdots \quad (50)$$

If Λ' and Λ'' are both greater than zero, R_{ij} stands for R_{cc} and R_{dd} (usually written R_c and R_d) if $\Delta\Lambda = 0$, or for R_{cd} and R_{dc} if $\Delta\Lambda = \pm 1$.[64,65] The relation of the subscripts c and d to the designations of the rotational levels can be seen from Fig. 17. The lines $R_c(M)$ and $R_d(M)$, or $R_{cd}(M)$ and $R_{dc}(M)$, form a (usually narrow) doublet. If either Λ' or Λ'' is zero,[64] only a single R line is present for each value of M, and the simple symbol $R(M)$ is used. It should be noted that the M values, like the J values, are integral.

---

[63] The designations "positive branch" and "positive term" have no relation to each other.

[64] This statement applies to ordinary (case b') singlet states and to case a states, but not in case c. In case c it must be modified by inserting Ω' and Ω'' in place of Λ' and Λ'' (cf. section H1).

[65] Symbols such as R_{cd} and R_{dc} can if desired be simplified to R_d and R_c respectively, it being then understood that the subscript refers only to the *lower* of the two energy levels involved. This convention is analogous to that whereby one gives only J'' (abbreviated as J), and not J', in such symbols as $R_c(J)$. The proper subscript c or d for the upper level can always be determined by means of the selection rule that positive rotational levels combine only with negative levels, and vice versa. There are to be sure occasional violations of this selection rule, as for example in some of the satellite branches in the OH bands.[60] In such cases the double subscripts must be used.

Similarly for the P branch or branches, putting $J'=J''-1$ in Eq. (49) and then substituting $M=-J''$, one gets

$$P_{ij}(M) = \nu_0 + (B' + B'')M + (B' - B'' + D' - D'')M^2 + \phi_i'(-M-1) - \phi_j''(-M) + 2(D' + D'')M^3 + (D' - D'')M^4 + \cdots \tag{51}$$

P_{ij} stands for P_c and P_d if $\Delta\Lambda=0$ or for P_{cd} and P_{dc} if $\Delta\Lambda=\pm 1$, or for P if Λ' or Λ'' is zero. If we have two P lines for each M value, these form a (usually narrow) doublet.

In so far as we can neglect the small functions ϕ' and ϕ'', branches such as $R_{cd}(M)$ and $R_{dc}(M)$, if both present, are coalescent, and likewise branches such as $P_{cd}(M)$ and $P_{dc}(M)$. Hence when ϕ' and ϕ'' are negligible, we always have in effect a single P branch and a single R branch. Further, Eqs. (50) and (51) for these P and R branches both become identical with Eq. (11) of Part I (except that ν_0 differs by a small additive constant from ν_0 of Eq. 11), and the two branches form a single series just like the P–R series of the $^1\Sigma,^1\Sigma$ bands in Part I.

For the Q branch or branches, the following equation is obtained by putting $J'=J''$ in Eq. (49), and also substituting M for J'':

$$Q_{ij}(M) = \nu_0 + (B' - B'')M + (B' - B'' + D' - D'')M^2 + \phi_i'(M) - \phi_j''(M) + 2(D' - D'')M^3 + (D' - D'')M^4 + \cdots . \tag{52}$$

If Λ' and $\Lambda''>0$, Q_{ij} stands for Q_{cd} and Q_{dc} if $\Delta\Lambda=0$ or for Q_c and Q_d if $\Delta\Lambda=\pm 1$, while if either Λ' or Λ'' is zero only one branch is present,[64] and the subscripts are usually dropped. If there are two Q lines for each M value, they form a (usually narrow) doublet.

The manner in which the structure depends on B', B'', D', and D'' is the same in any case a or c or singlet band as in the special case $^1\Sigma\rightarrow{}^1\Sigma$ (cf. Part I, pp. 71–72). The factors governing the formation of band-heads in P or R branches are also the same as in $^1\Sigma\rightarrow{}^1\Sigma$ transitions (Part I, pp. 73–4). The same is true of the factors which determine the arrangement and relative intensities of different bands (cf. Part I). A new feature, however, in bands where $\Delta\Lambda=\pm 1$, is that the beginning of the Q branch often functions as a band-head because of the crowding together of lines there, even though these lines are usually weak (cf. Figs. 18, 19). Thus each such band has two heads. Further, in bands with double P and R branches (Λ' and Λ'' both greater than zero), the P or R head should appear double in case the doublet widths in the band-lines are large.

Although the M numbering used in Eqs. (50)–(52) is convenient in discussing band structures, another numbering in which the value of J'' is given in parentheses, as e.g. in $P(2)$, $Q(1)$, $R(3)$, is usual in referring to band lines in the analysis of band spectra (cf. Fig. 2 and pp. 70–71 of Part I, Fig. 17, etc.)

3. *Intensity relations and missing lines.* The empirical structure and appearance of any band depend jointly on the arrangement of the lines (Eqs. 50–52) and on their relative intensities. (Cf. Part I, last paragraph of p. 69,

et seq, for a discussion of this dependence.) The theoretical emission intensities I or absorption coefficients α for the lines of an emission or absorption band are given by the set of equations (53)–(55).[66]

$$\text{Emission band-lines: } I = k\nu^4 iR' \tag{53a}$$

$$\text{Absorption band-lines: } \alpha = (k/8\pi hc)\nu iR''. \tag{53b}$$

In these equations, k is (very nearly[10]) a constant in any one band, but differs from one band to another, ν is the wave-number of the line, h and c are Planck's constant and the velocity of light, and i is a function of the rotational quantum number (cf. Eqs. 54–55). R is equal to N/p, where N is the total number of molecules at any moment in the proper initial state for *emission*, or, the number of molecules *per cc* in the proper initial state for *absorption*, and $p(=2J+1)$ is the statistical weight of the initial state. The factor ν or ν^4 can usually be treated as constant in comparing different lines in a single band. (In Eqs. 12 and 13 of Part I this was done.)

If the initial distribution is one corresponding to thermal equilibrium at some definite temperature T, the factor R in Eq. (53*a*) or (53*b*) becomes proportional to the Boltzmann factor $e^{-E/kT}$. Here E can be written $E=E_e+E_v+E_r$. In any one band (v' and v'' fixed), E_v is always a constant or practically so. In singlet and case c bands E_e is also a constant, so that $e^{-E/kT}$ reduces to a constant times $e^{-E_r/kT}$. The same is (at least approximately) true in case b. In case a multiplets each band is composed of two or more sub-bands (same v', v'', different Σ). When the multiplets are widely spaced the sub-bands are widely separated and are better considered as separate bands belonging to different sub-systems of a multiplet band-system (cf. section *G*1). In such bands we have $E_e=E_0^e+A\Lambda\Sigma$. From the foregoing we see that for thermal equilibrium Eqs. (53*a*) and (53*b*) can always be written as follows:

$$\text{Emission band-lines: } I = g'\nu^4 ie^{-E_r'/kT} \tag{53c}$$

$$\text{Absorption band-lines: } \alpha = g''\nu ie^{-E_r''/kT}. \tag{53d}$$

In these equations, g is (very nearly[10]) a constant in any one band in case b or c or singlet spectra, or in any one sub-band in case a multiplet spectra.

Very often in emission bands the initial distribution of molecules among different rotational levels of a given electronic and vibrational state is approximately of a type corresponding to thermal equilibrium, even when the excitation is not thermal in character (cf. Part I, p. 69 and Ref. 9, also Ornstein and Van Wijk,[84] and Kapuściński and Eymers[98]), and even when the distribution between different vibrational or electronic states is not at all

---

[66] I is in ergs per sec, while α is defined by the equation $J=J_0e^{-\alpha x}$, where x is the length of path through which a light beam has passed when its intensity has been reduced from J_0 to J. For a review of the bases of Eqs. (53), reference may be made to Ruark and Urey's "Atoms, Molecules, and Quanta," pp. 697–8 (McGraw Hill, 1930).

In connection with the derivation of Eqs. (54)–(55) reference may be made to pp. 716–17 of the same book, and to H. Hönl and F. London, Zeits. f. Physik **33**, 803 (1925); also (quantum mechanics), to J. H. Van Vleck, Phys. Rev. **33**, 467–506 (1929), especially pp. 475–6 and references there given.

like that for thermal equilibrium at the temperature indicated by the rotational distributions. In multiplet bands, for example, the experimental g' factors may be nearly the same for different multiplet components when for thermal equilibrium they would differ in proportion to $e^{-A\Lambda\Sigma/kT}$, a quantity which in practise may have values differing greatly from unity. A good example of this situation is found in the HgH bands (cf. section *J2c*).

Under special conditions (e.g. excitation by monochromatic light or by impacts of the second kind or by electrons of closely regulated velocity) the function R in Eq. (53*a*) may of course have values entirely different from those for thermal equilibrium.

The i factors in Eqs. (53) are independent of excitation conditions, and are given by Eqs. (54)–(55):

$$\Omega' = \Omega'' \text{ and } J' = J'',\ i = (4J+2)\Omega^2/J(J+1) \tag{54a}$$

$$\Omega' = \Omega'' \text{ and } J' = J'' \pm 1,\ i = 2J - 2\Omega^2/J \tag{54b}$$

$$\Omega' = \Omega'' \pm 1 \text{ and } J' = J'',\ i = (2J+1)(J+\Omega)(J-\Omega+1)/J(J+1) \tag{55a}$$

$$\Omega' = \Omega'' \pm 1 \text{ and } J' - J'' = \Omega' - \Omega'',\ i = (J+\Omega)(J+\Omega-1)/J \tag{55b}$$

$$\Omega' = \Omega'' \pm 1 \text{ and } J' - J'' = \Omega'' - \Omega',\ i = (J-\Omega)(J-\Omega+1)/J. \tag{55c}$$

In Eqs. (54) and (55), the symbol J means the larger of the two quantities J' and J'', if these are unequal. The symbol Ω has analogous meanings. When $\Lambda'>0$ and at the same time $\Lambda''>0$, each line is double, the two components having the *same value of i*.[67] In this case Eqs. (54)–(55) give the sum of the i values of the two components.

In the single series of lines which the P and R branches together make when the ϕ's are neglected (cf. above),[68] one or more lines near and always including $M=0$ are missing. One or more lines corresponding to the lowest M values, and always including $M=0$, are also missing in the Q branch or branches. The missing lines are determined by the conditions $J'\geq\Omega', J''\geq\Omega''$ (cf. Part II*b*, p. 105). The various missing lines, the intensity distribution among the band lines, and the effects of the Λ-type doubling when the ϕ's are not neglected, depend in a very characteristic manner on the values of Ω' and Ω''.

The relations discussed above can best be appreciated by a study of the examples in Figs. 17–19. It will be noted that in these examples the energy-level Λ-type doublet widths $\phi_c(J)-\phi_d(J)$ are shown as having very varied behavior, depending essentially on the value of Ω. The $\phi(J)$'s and their effects on the band structure will be discussed in some detail in the following sections (for a brief discussion, cf. Part II*b*, pp. 99–106 and Fig. 16 and recent revision[55] of pp. 99–100.)

---

[67] In each Λ-type doublet rotational level (or in each Ω-type doublet level, in case *c*), the two components have equal statistical weight. Hence in the resulting double lines (cf. Fig. 17), taking into account also the equality of the i values, the two doublet components should be of practically equal intensity, at least under usual conditions of excitation.

[68] As will be shown below, branches such as P_c and R_c, or P_d and R_d, may still form a single series even when we do not neglect ϕ' and ϕ'': cf. Eq. (58) for the case of singlet states.

F. SINGLET AND CASE b' BANDS

In the preceding section, we have been considering relations which hold equally for case c, case a, and singlet or case b' bands. In the present section, we shall consider exclusively singlet and case b' bands, with particular reference to the $\phi(J)$'s and their relation to rotational uncoupling of the L vector (approach to case d'). In Sections G and H we shall then consider several special features of the bands and band-systems of case a multiplet states and of case c states.

1. *General.* In Fig. 17 the arrangement of the rotational levels and their relation to the band lines are shown for several important types of singlet bands. Empirically, the following types are now known: $^1\Sigma,^1\Sigma$; $^1\Pi,^1\Sigma$; $^1\Sigma,^1\Pi$; $^1\Pi,^1\Pi$; $^1\Delta,^1\Pi$. All of these, it will be noted, are in agreement with the selection rule $\Delta\Lambda=0,\pm 1$. Fig. 17 and the entire discussion of this section (F) apply equally well to case b' bands with $S>0$, provided first we substitute Λ and K everywhere in the text for Ω and J; the superscripts 1 should also be dropped in symbols such as $^1\Sigma,^1\Pi,^1\Delta$.

In Fig. 18 the characteristic missing lines and the intensity relations are shown for the band types of Fig. 17. In Fig. 17 we use the Λ and K notation of case b' in order to facilitate the subsequent discussion of case b states. Fig. 19 shows again, by means of another type of diagram, first used by Fortrat, the missing lines and intensity relations for a $^1\Pi,^1\Sigma$ transition. Fortrat diagrams show well the forms of the branches as functions of M. These are always parabolic arcs, if we neglect small terms in M^3,M^4, etc. in Eqs. (50)–(52). The band-head appears at or near the vertex of the P parabola if $B'>B''$ or of the R parabola if $B'<B''$. The vertex of the Q parabola is usually also noticeable in the band as a well-marked second head, especially if the low-numbered Q lines are strong (B large or T low).

In connection with Fig. 17, we note that $^1\Sigma,^1\Sigma$ transitions are of two kinds, namely $^1\Sigma^+,^1\Sigma^+$ and $^1\Sigma^-,^1\Sigma^-$.[69] Empirically there is no difference between these. They have been treated in detail in Part I under the name of $^1\Sigma,^1\Sigma$ transitions.[70]

2. *Effects of uncoupling terms $\phi(J)$ for small uncoupling.* Theory and experiment indicate[71] that, so long as $\phi(J)$ is small, it can be closely approximated, for singlet states,[55] by the series

---

[69] Transitions $^1\Sigma^+$, $^1\Sigma^-$ and $^1\Sigma^-$, $^1\Sigma^+$ are not possible, because of the joint action of (1) the rule that only positive and negative terms can combine and (2) the rule $\Delta J=\pm 1$ only (no Q branches) which holds when $\Omega'=\Omega''=0$ (cf. Eq. 54a). [For exactly the same reasons, 0^+, 0^- and 0^-, 0^+ transitions (cf. section $H2$) are ruled out in case c.] In $^1\Sigma$, $^1\Sigma$ bands a departure of the coupling conditions from those of case b' toward case d' or toward case c is capable, however, of breaking down the second rule and permitting weak Q branch transitions between $^1\Sigma^+$ and $^1\Sigma^-$ states. [Similarly in 0,0 bands (case c) a departure of the coupling relations from those of case c toward b' or d' should make possible 0^+, 0^- and 0^-, 0^+ bands composed of weak Q branches.]

[70] A slight refinement, of no practical importance, is the fact that ν_0 is now seen to be slightly different from $\nu_e+\nu_v$. This was not noted in the discussion in Part I.

[71] Theory of Λ-type *doublet separations* $\phi_c(J)-\phi_d(J)$, R. de L. Kronig, Zeits. f. Physik **50**, 356 (1928); J. H. Van Vleck, Phys. Rev. **33**, 484–9 (1929). Theoretical deduction of forms

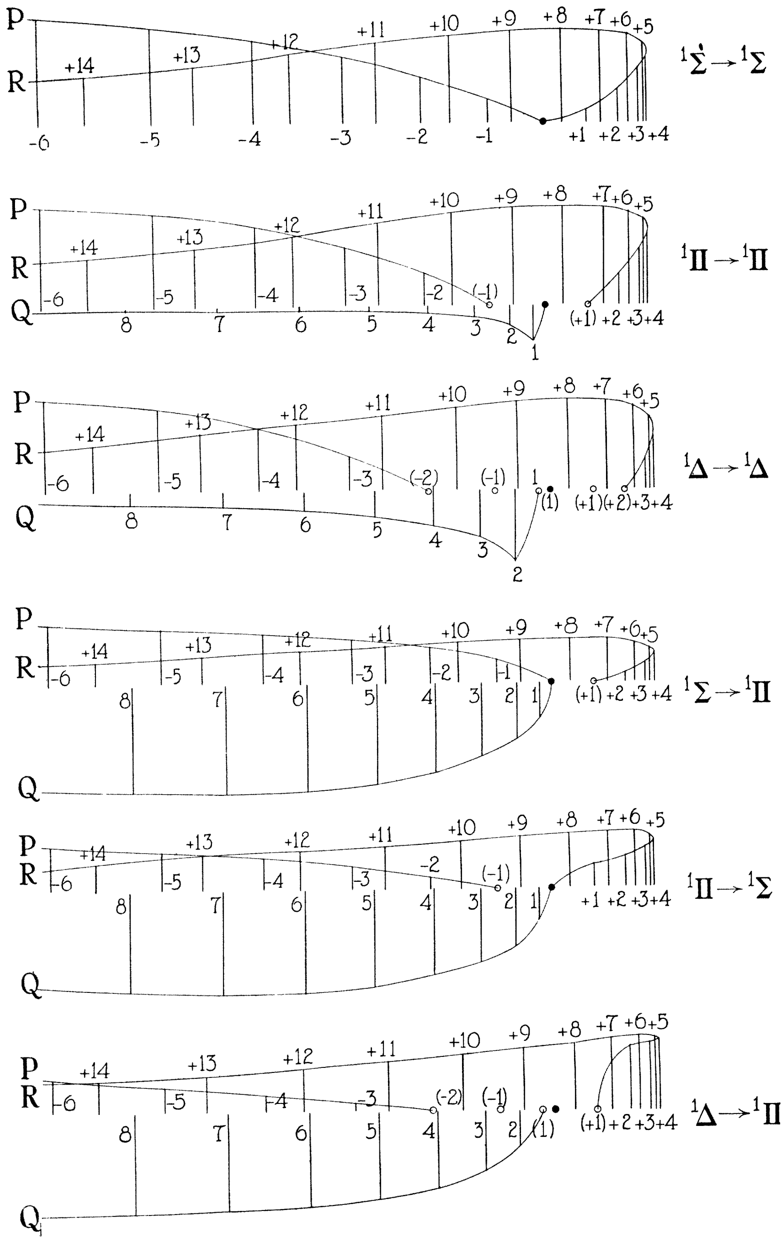


Fig. 18. Missing lines and intensity distributions in singlet bands. The heights of the lines represent their intensities. In the $^1\Pi \rightarrow {}^1\Pi$, $^1\Delta \rightarrow {}^1\Delta$, and $^1\Delta \rightarrow {}^1\Pi$ bands the lines are really all double. The direction of increasing frequency is towards the right. The central missing line ($M=0$, $\nu=\nu_0$ in Eqs. 50 and 51) is shown by a black circle (●), the other missing lines by light circles (○). The numbering of all the lines is in terms of M values.

The intensities were calculated according to Eqs. (53*c*) and (54)–(55), assuming $T=300°\,K$. The wave numbers of the lines were calculated according to Eqs. (50)–(52), assuming $B'=1.85$, $B''=2.35$, $D'=D''=0$, $\phi'=\phi''=0$. The way in which the appearance of the bands would vary with different values of B', B'', T, etc., can be judged by a study of Figs. 3 and 4 of Part I.

$$\phi_i(J) = \kappa_i + \delta_i J(J+1) + \mu_i J^2(J+1)^2 + \cdots, \qquad (56)$$

where $\delta_i >> \mu_i >> \cdots$, and κ_i is of the order of magnitude of δ_i. In the case of ${}^1\Sigma$ states, $\phi(J)$ is single valued, but if $\Lambda > 0$ it is double-valued (ϕ_c and ϕ_d). When the $\phi(J)$'s are given by Eq. (56), they can be amalgamated very easily with the other terms in Eqs. (29), (31), (49), and (50)–(52). If we put[55]

$$B^x{}_i = B_v + \delta_i,\; D^x{}_i = D_v + \mu_i, \qquad (57)$$

then in the above mentioned equations we can omit all the functions $\phi(J)$ if at the same time we replace all the B_v's and D_v's by corresponding B^x's and D^x's. For example, Eqs. (50)–(52) become

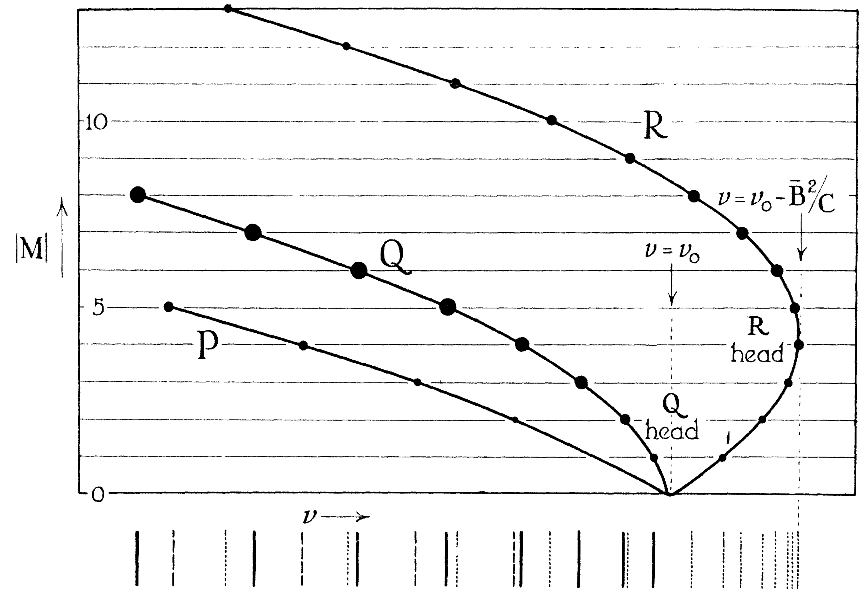


Fig. 19. Fortrat diagram of a ${}^1\Pi, {}^1\Sigma$ band. (The diagram also applies equally well to any case b' Π,Σ band.) *Above*, Eqs. (50), (51) and (52) for ν are plotted as continuous functions of $|M|$. In the P branch, $M = -K''$, hence $|M| = K''$; in the Q branch, $M = K''$; in the R branch, $M = K''+1 = K'$. If ν were plotted against M instead of against $|M|$ the P and R branches would form a continuous curve. The wave-numbers of actual band-lines are given by the intersections of the plotted approximately parabolic curves with horizontal lines corresponding to integral values of $|M|$. The intensities of the band-lines are indicated here by the areas of the black discs which have been drawn at each such intersection. Missing lines are indicated by the absence of a disc. The values of B', B'', and T assumed here are the same as for ${}^1\Pi, {}^1\Sigma$ in Fig. 18, and the frequencies and intensities are the same as in Fig. 18. *Below*, the appearance of the actual band is shown, using unbroken lines for the Q branch, broken lines for the P branch, and dotted lines for the R branch.

---

of *individual* $\phi_i(J)$'s of ${}^1\Sigma$, ${}^1\Pi$, and ${}^1\Delta$ states for the case of a special model (especially appropriate to the excited states of H_2 and He_2), E. L. Hill and J. H. Van Vleck, Phys. Rev. **32,** 270 (1928); G. H. Dieke, Zeits. f. Physik **57,** 71 (1929). Summary of experimental data (on states with $\Lambda > 0$), R. S. Mulliken, Phys. Rev. **33,** 507–11 (1929); Phys. Rev. 1931.

$$\left.\begin{matrix} P_{ij}(M) \\ R_{ij}(M) \end{matrix}\right\} = \nu_0 - (B^x{}_i{}' + B^x{}_j{}'')M + (B^x{}_i{}' - B^x{}_j{}'' + D^x{}_i{}' - D^x{}_j{}'')M^2 + 2(D^x{}_i{}' + D^x{}_j{}'')M^3 + (D^x{}_i{}' - D^x{}_j{}'')M^4 + \cdots \tag{58}$$

$$Q_{ij}(M) = \nu_0 + (B^x{}_i{}' - B^x{}_j{}'')M + (B^x{}_i{}' - B^x{}_j{}'' + D^x{}_i{}' - D^x{}_j{}'')M^2 + 2(D^x{}_i{}' - D^x{}_j{}'')M^3 + (D^x{}_i{}' - D^x{}_j{}'')M^4 + \cdots . \tag{59}$$

In using Eqs. (58) and (59), it should be recalled that in a given band we have P_c, P_d, Q_{cd}, Q_{dc}, R_c, R_d branches or else P_{cd}, P_{dc}, Q_c, Q_d, R_{cd}, R_{dc} branches or else just one P, one Q, and one R branch.

The *form* of Eqs. (58)–(59)—that of Eq. (58) is the same as that of Eq. (11)—is exactly the same as if the ϕ's had all been zero in Eq. (49). But we see that the "effective" B and D values B^x and D^x, which determine the band structure and which we can obtain from its analysis, are not the true B_v's and D_v's which we need in calculating I_e, r_e, etc. Furthermore, there is usually no way of determining just how much the δ's and μ's contribute to the effective B's and D's. Fortunately, however, the theory gives us assurance that these contributions are always small in cases for which Eq. (56) holds. What happens when this is not true we shall consider a little later.

In the case of $^1\Pi$ states, as Van Vleck has shown,[71] the function $\phi_i(J)$ has the two forms

$$\phi_d(J) = -2C + (C + C_1)J(J+1) + \cdots , \text{ and,}$$
$$\phi_c(J) = -2C + (C + C_2)J(J+1) + \cdots . \tag{60}$$

[A letter from Van Vleck shows that ϕ_d goes with C_1.] In general, the theoretical determination of the coefficients C requires a knowledge of all the $^1\Sigma$ and $^1\Delta$ states of the molecule, and is therefore not practicable. But for the special case that the uncoupling terms $\phi(J)$ are due mainly to the presence of an electron in a large orbit with azimuthal quantum number l (example of the case of "*pure precession*"), as in many of the states of H_2 and He_2, simple formulas can be given for the C's (cf. Van Vleck, and Dieke[71]). C_2 is always zero in this case, and if $l=1$, C is also zero, so that one of the two ϕ's is also zero, and one of the two B^x's is equal to B_v. This case is found experimentally in the $np\Pi$ levels of He_2, of which a long series is known ($n=2$ to 11). When one compares the $B^x{}_i$ values for different members of this series, it is observed that B^x_c remains nearly constant, while B^x_d decreases steadily with increasing n. We conclude that $B^x_c = B_v$ and that $B^x_d = B_v + C_1$. The B_v values so obtained vary only slightly with n, as is to be expected since the equilibrium of the nuclei is very little affected by the excited electron in its large orbit. The C_1 values agree well with those calculated theoretically.—Fig. 13 of Part II*b* corresponds to the case just discussed, except that here (in He_2) the Σ levels are above the corresponding Π levels instead of below them as in Fig. 13.

For the case of pure precession, $\phi(J)$ is zero for $^1\Sigma$ states if $l=0$, but if $l=1$, it is comparable with the $\phi(J)$'s of $^1\Pi$ states, and if $l=2$, with those of $^1\Delta$ states.

For $^1\Delta$ states the theoretical expressions for the coefficients in $\phi_i(J)$ in

Eq. (56) are in general very complicated, but for the case of pure precession and a special (qualitatively correct) model they have been evaluated.[71]

Although simple theoretical formulas cannot be given in general for the coefficients of Eq. (56), theoretical expressions are available when $\Lambda > 0$ for the *differences* $\phi_c(J) - \phi_d(J)$, and these differences can also be determined experimentally.

The theory shows that for $^1\Pi$ states, $\delta_c - \delta_d$ (equal to $C_2 - C_1$ of Eq. 60) is of the same order of magnitude as δ_c or δ_d itself, so that the Λ-type doublet widths in the rotational levels of such states are given by

$$^1\Pi \text{ states, } \Delta\nu_{cd} = (\delta_c - \delta_d)J(J+1) + \cdots . \qquad (61)$$

For $^1\Delta$ states, the theory gives $\delta_c - \delta_d \sim 0$, but gives $\mu_c - \mu_d$ comparable with μ_c or μ_d.[72] The Λ-type doublets should therefore be very much narrower than in $^1\Pi$ states, being given[72] by

$$^1\Delta \text{ states, } \Delta\nu_{cd} = (\mu_c - \mu_d)J^2(J+1)^2 + \cdots . \qquad (62)$$

The theory further shows that $\delta_c \sim \delta_d$, $\mu_c \sim \mu_d$ for $^1\Phi$ states $(\Lambda = 3)$, giving still smaller $\Delta\nu$'s proportional to $J^3(J+1)^3$; and so on.

The effect of Λ-type doubling is obvious in the band-lines themselves only when Λ' and Λ'' are both greater than zero; then each line is double. The Λ-type doublet widths in the band-lines are always either the sum or the difference of the Λ-type doublet widths of the upper and lower energy levels involved. If in the Q branches the line doublet widths are *sums* of energy-level doublet widths, then in the P and R branches they are *differences* of energy-level doublets, and vice versa. This and certain further relations can be better understood from the diagrams in Figs. 22 and 34*b*. These figures, to be sure, do not show singlet bands, but the relations in question are equally well exemplified in multiplet bands. (It is also worth noting that the $^3\Pi_1$, $^3\Pi_1$ diagram in Fig. 22 could have been used equally well as a $^1\Pi$, $^1\Pi$ diagram.) Equations for the line doublet widths can easily be obtained from Eqs. (57)–(59), but these are somewhat complicated and it does not seem worth while to give them here.

3. *Effects of stronger uncoupling; case d' and intermediate cases.* As we have seen in Part II*b* (Ref.54, pp. 100–104, and Ref. 55), the terms $\phi_i(J)$ in singlet states are symptomatic of the beginning of an uncoupling of an orbital angular momentum vector L^* from the electric axis of the molecule whereby an average component $ph/2\pi$ of L^* parallel to the axis of rotation is developed. So long as $\rho << L$, the energy is approximately given, as we have seen, by $T = A + B^x J(J+1)$. When the uncoupling becomes practically *complete* (case d'), ρ becomes nearly constant and of the same order of magnitude as L, and the energy is approximately given by

$$T = A^0 + B(J - r)(J - r + 1) = A^* + \epsilon J + BJ(J+1),$$

---

[72] More precisely[71], the doubling in $^1\Delta$ states is proportional to $(J-1)J(J+1)(J+2)$, which means that $\delta_c - \delta_d = -2(\mu_c - \mu_d)$, but this times $J(J+1)$ is negligible.

where $J-r=R$ of Eq. (30) of Part II*b*, and r is a small integer approximately equal to ρ. During intermediate stages of uncoupling, the energy cannot well be expressed over a range of J values by a power series in J.[73] If the uncoupling does not proceed very far, however, the following expression can be used:

$$\phi_i(J) = \kappa_i + \epsilon_i J + \delta_i J(J+1) + \eta_i J^3 + \cdots . \tag{63}$$

Relations corresponding to Eq. (63) have been found especially in some of the $p\Pi$ levels of He_2 which show only moderate uncoupling, and also in other cases, e.g. that of the $^1\Sigma$ upper electron level of the well-known CuH bands.[12]

If we use Eq. (63) instead of Eq. (56) for the $\phi(J)$'s in Eq. (49), the following equations are found for the P and R branches:

$$R_{ij}(M) = (\nu_0 + \epsilon_j'') + (B^x{}_i' + B^x{}_j'' + \epsilon_i' - \epsilon_j'')M$$

$$+(\text{terms as in Eq. 59, if we neglect the } \eta_i\text{'s of Eq. 63}) \tag{64}$$

$$P_{ij}(M) = (\nu_0 - \epsilon_i') + (B^x{}_i' + B^x{}_j'' - \epsilon_i' + \epsilon_j'')M + \cdots . \tag{65}$$

The P_c and R_c (or P_d and R_d, or P_{cd} and R_{cd}, or P_{dc} and R_{dc}) branches no longer form a single series as they did in Eq. (58). In addition to the fact that the coefficients of M (and M^2, etc.) are different for P and R, the two branches do not coincide at the missing line $M=0$. Relations of this kind are found in the He_2 and CuH bands just mentioned.

If we go now to the case of complete uncoupling (case d'), we have the rotational quantum vector R^* combining with the vector l^* or L^* to give a resultant J^*. Since in case d' the interaction between R^* and the motions of the electrons is small, the probability of simultaneous changes in the nuclear and electronic quantum numbers is nearly zero, according to classical electromagnetic theory (using Fourier analysis) applied via the correspondence principle to quantum theory. Hence we expect either (*a*)$\Delta R = \pm 1$ (and $\Delta J = 0, \pm 1$), with no changes in the electronic quantum numbers (pure rotation or oscillation-rotation bands) or (*b*)$\Delta R = 0$ (and $\Delta J = 0, \pm 1$) if the electronic quantum numbers change (electronic bands); in (*b*) the same selection rules hold for l or L as in atoms ($\Delta l = \pm 1$, or $\Delta L = 0, \pm 1$). If in Eq. (30) of Part II*b*, the term $f(R, K-R)$ is negligible, we have, taking $\nu = T' - T''$,

$$T' = T_e' + G' + B'R'(R'+1) + \cdots ,$$

$$T'' = T_e'' + G'' + B''R''(R''+1) + \cdots ,$$

and, calling $R' = R'' = M$,

$$\nu = \nu_0 + (B' - B'')M + (B' - B'')M^2 + \cdots . \tag{66}$$

This has the form of an ordinary Q branch (cf. Eq. 52), regardless of the value of ΔJ. In practise, $f'(R,K\text{-}R)$ and $f''(R,K\text{-}R)$ are not entirely negligible, and we expect a group of branches differing in form somewhat, or even considerably (depending on f' and f'') from that of a Q branch.[73] How many branches there are in such a group depends on the values of L' and L''; e.g., if $L'=2$, $L''=1$, there are nine.

As was noted in Part II*b*, examples of case d' states are known only in some of the higher excited electron levels of H_2 and He_2. No bands are yet known, however, in which both the initial and final states are case d'. In many bands the upper level is, or approximates, case d', while the lower is case b' with a more or less strong departure toward d'. In such bands the forms and intensity distributions of the branches show many peculiarities, and vary in a remarkable manner from one example to another. For example, a single branch may have two heads.[74] Many of the branches which would occur for case b' are contrary to the selection rules of case d', and even in the intermediate cases under discussion these are generally weak or absent. On the other hand, some branches which are absent or weak in case b' become strong. Even in those bands where both the upper and the lower level approximate case b', the tendency toward case d' gives rise to considerable deformations in the branches, as already discussed, and causes very noticeable changes in the intensity relations as compared with Eqs. (54)–(55).[73]

G. CASE *a* MULTIPLET BANDS

1. *Bands and sub-bands; systems and sub-systems.* Before taking up band structures for case *a* multiplet bands it is well to consider how the bands are arranged in the spectrum. In a transition between two case *a* multiplet levels, the selection rules for the electronic quantum numbers are $\Delta\Lambda=0$, ± 1 and $\Delta\Sigma=0$ (cf. section *D*2). Because of $\Delta\Sigma=0$ the resulting molecular multiplet contains the same number of members ($2S+1$, one for each Σ value) as do the multiplet levels themselves, whereas in atomic multiplets the number of components in the multiplet is in general greater than the number of members in either of the two levels. If the magnitude of the coupling constant A (cf. Eqs. 27 and 31) is not very large, the band lines corresponding to a given v' and v'', but belonging to different members of a multiplet, are closely associated and may be considered as together forming a multiple band,—the (v', v'') band,—of which they form *sub-bands* (cf. Fig. 20*a*). If $|A|$ is large compared with the vibrational coefficients ω_e' and ω_e'', however, then band-lines alike in v' and v'' but belonging to different multiplet components may be far apart and form in fact separate bands (cf. Fig. 20*b*), and the sets of such bands associated with each component of the multiplet are quite naturally regarded as constituting separate band-systems or as forming sub-systems of a multiple system. [On p. 68 of Part I we defined a band-system as consisting of all the spectrum lines associated with a definite pair of electronic states. It is natural to consider all the members of a molecular mul-

---

[73] For a more exact discussion of the energy and intensity relations in case d' and intermediate cases, and their relation to the observational material on He_2, cf. G. H. Dieke (*l. c.* Ref. 71), and R. de L. Kronig and Y. Fujioka, Zeits. f. Physik, **63**, 168, 175 (1930).

[74] For a review of the empirical material on He_2, cf. W. E. Curtis, Trans. Far. Soc., **25**, Part 11, p. 694 (1929).

tiplet as belonging to a single "electronic state," and the corresponding bands as forming a single system, so long as $|A|$ is not too large (case *b* and, for not too large $|A|$ values, case *a*). But when $|A|$ is large (case *a* with large $|A|$, and case *c*,—cf. section *H*1), it is more natural to regard different multiplet components as separate "electronic states," and the corresponding bands as forming separate systems.]

The arrangement of sub-bands in a band, or of sub-systems in a system, is capable, in respect to the relations of sub-bands or sub-systems to energy levels, of showing a number of variations which are important from the standpoint of the experimentalist. These depend on the relative values of A' and A''. They are illustrated in Fig. 21.

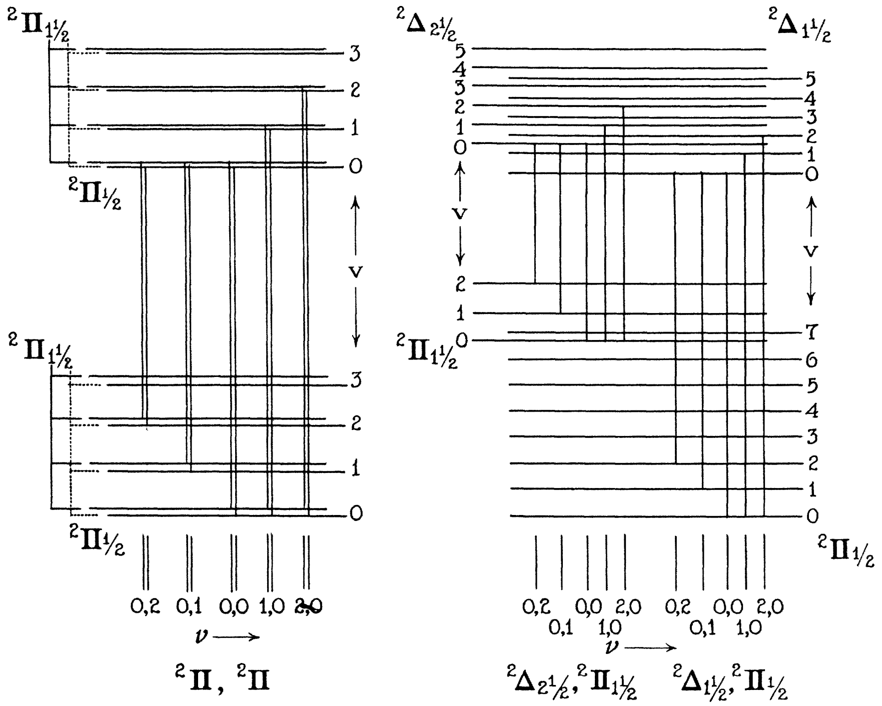


Fig. 20. In Fig. 20*a* is shown a $^2\Pi,^2\Pi$ system composed of bands each consisting of two overlapping sub-bands. In Fig. 20*b* is shown a $^2\Delta,^2\Pi$ system consisting of two sub-systems $^2\Delta_{2\frac{1}{2}},^2\Pi_{1\frac{1}{2}}$ and $^2\Delta_{1\frac{1}{2}},^2\Pi_{\frac{1}{2}}$ which act nearly like independent systems, although if more bands were shown, they would overlap somewhat.

2. *Band structures in case a and their interpretation.* Fig. 22 shows the nature of the band-structures, missing lines, and intensity relations for some typical examples of case *a* bands. It is based on relations already discussed (cf. sections *E*2 and *E*3, noting especially the paragraph before Eqs. 53*c*,*d*), except as concerns the forms of the $\phi(J)$'s. These are treated below.

In connection with the interpretation of case *a* bands it should always be borne in mind that the ideal case *a* is not often closely approached. This is because if $|A|$ is too large we get tendencies toward case *c*, while if it is too small, or in any case if J is large, we approach case *b*. Reference should be made to section *H3* for a detailed discussion of these deviations (cf. also *G4*).

In the analysis of case *a* bands the apparent or effective B and D values obtained may be expected to differ from B_v and D_v values for two reasons: (1) the effect of the tendency toward case *b* (S uncoupling) causes the B_v and D_v values to be replaced by the quantities B^* and D^*, and (2) the effect of the $\phi(J)$'s causes these in turn to be replaced by B^{*x} and D^{*x}. ($B^{*x}{}_i = B^* + \delta_i$, etc.—cf. Eq. 57). Fortunately allowance can be made, in the case of the B's, for the first of these effects, which is usually much the more important, by means of the relation $B^* = B_v(1 \pm B_v/A\Lambda + \cdots)$ for doublet states (cf. Eq. 46) and by means of the following relation for triplet states:[76]

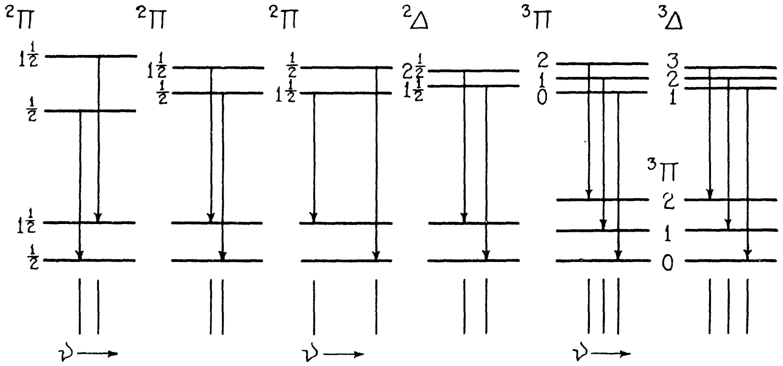


Fig. 21. Diagrams illustrating, by examples of $^2\Pi, ^2\Pi$ and other transitions, how the relative ν values of the different components of a case *a* molecular multiplet depend on $A' - A''$. The diagrams correspond to molecules without vibration or rotation. The numbers given are the Ω values of the various levels. For each of the examples shown, two cases are possible which empirically are decidedly different, namely (1) bands degraded toward higher frequencies, (2) bands degraded toward lower frequencies. A further cause of differentiation of empirical structure (magnitude of $A' - A''$ relative to ω_e' or ω_e'') is illustrated in Fig. 20.

$$\text{For } \Sigma = 0,\ B^* = B_v;\ \text{for } \Sigma = \pm 1,\ B^* = B_v(1 \pm 2B_v/A\Lambda + \cdots). \qquad (67)$$

3. *$\phi(J)$'s and Λ-type doubling in case a.* For case *a* triplet bands[75] (or in general, for bands where S is integral), the $\phi_i(J)$'s, for small L uncoupling, are of the form given by Eq. (56). In case *a* the widths of the Λ-type doublets depend very strikingly on the value of Ω. Thus in $^3\Pi$ states (according to

---

[75] Theory ($^2\Pi$ and $^3\Pi$ states), cf. Van Vleck, *l. c.* Ref. 71; experimental data, cf. Mulliken, *l. c.* Ref. 71. Van Vleck gives for the most part only the relations for the Λ-type doublet widths, but the relations here given for the individual coefficients (in particular, δ_c and δ_d not necessarily both zero) are very probable when one considers the results of the calculations of Hill and Van Vleck and of Dieke (*l. c.* Ref. 71).

[76] Cf. E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 261 (1928). Eq. (67) follows from Hill and Van Vleck's equations for triplet states.

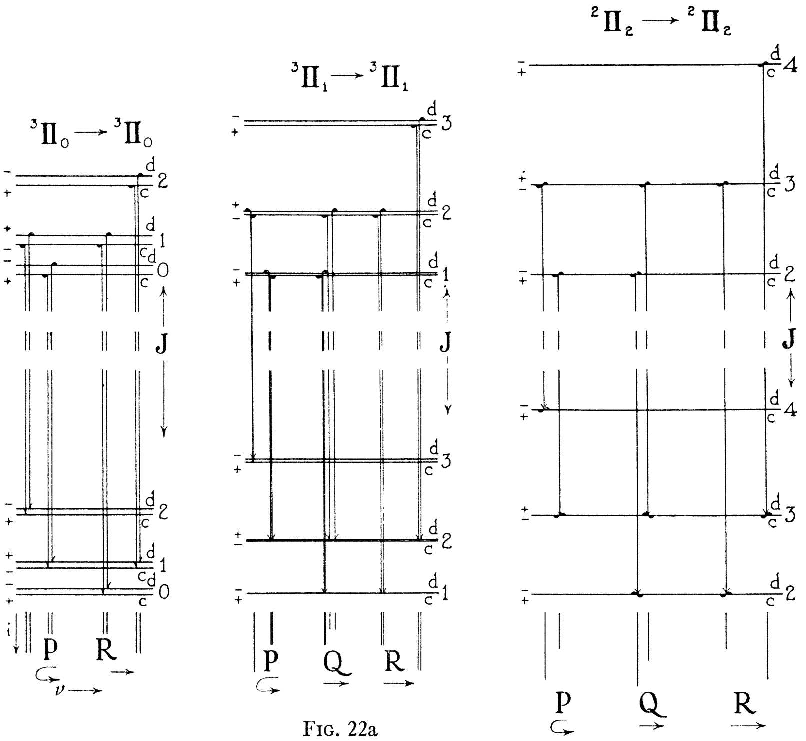


FIG. 22a

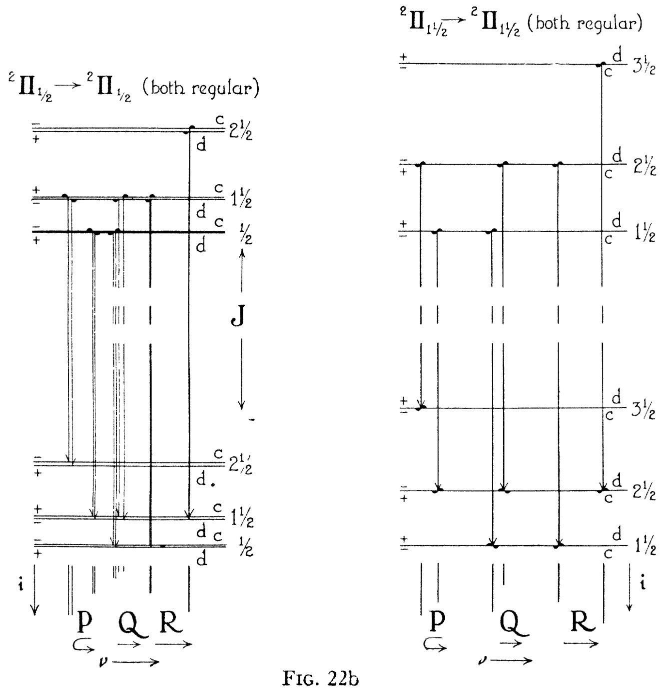


FIG. 22b

Fig. 22. First few rotational levels and first *two lines* in each branch, with their intensity factors i (cf. Eqs. 53-55) for several examples of transitions between case a states. The further course of the intensities in each branch can be seen from Eqs. (53)-(55). $B'=1.15B''$ has been arbitrarily assumed for the $^3\Pi$,$^3\Pi$ transitions and $B'=1.2B''$ for the $^2\Pi$,$^2\Pi$; this is merely to prevent the Q lines from falling together in the diagrams.

The relations between the $+$, $-$ and the c, d designations of the rotational levels are correctly shown (cf. Table V) in the diagram. The relations shown for the $^3\Pi$ states in Fig. 22 are equally applicable to regular and inverted $^3\Pi$ states. The relations shown for the $^2\Pi$ states are correct only for regular $^2\Pi$ states. For inverted $^2\Pi$ states the designations c and d must be interchanged (cf. Table V).

The order in which the c and d levels are drawn (i.e., d above or below c) is in the case of the $^2\Pi_{\frac{1}{2}}$ level that which is empirically usual for regular $^2\Pi_{\frac{1}{2}}$. In the case of the $^2\Pi_{1\frac{1}{2}}$ levels, the order shown is that which would be expected theoretically (cf. Fig. 16) to correspond to the order shown for $^2\Pi_{\frac{1}{2}}$, although experimental data on this relation are scanty because the Λ-type doublets are usually too narrow to measure in $^2\Pi_{1\frac{1}{2}}$. (The predicted relation has, however, been verified in some cases.) In the case of the $^3\Pi$ levels, the relations shown may not be typical; neither experimental data nor theory are yet sufficiently available to decide this.

The widths of the Λ-type doublets are arbitrary, but the mode of their variation with J is correct for case a states (cf. text, section *G*3): for $\Omega=0$, they are constant, for $\Omega=\frac{1}{2}$, they are proportional to $(J+\frac{1}{2})$, for $\Omega=1$, they are proportional to $J(J+1)$, for $\Omega=1\frac{1}{2}$ and 2 they are approximately proportional to J^3 and J^4 respectively. In the latter two cases they are ordinarily so small for small J values that they are not shown on the diagram. For diagrams of Λ-type doubling in $^3\Pi$ states intermediate between cases a and b, cf. Fig. 34b, neglecting the difference between light and heavy lines. The diagrams give a good idea of the varied manner in which the doublet widths in the band lines are related to the doublet widths in the energy levels. In particular, they show that the doublets may be very different in the P, Q, and R branches.

The diagram marked $^3\Pi_0$,$^3\Pi_0$ is equally applicable to any transition, for instance $^5\Pi_0$,$^5\Pi_0$, between case a states with $\Omega'=\Omega''=0$. The diagrams for $\Omega'=\Omega''>0$ are also applicable to any transition between case a or case c states with the same Ω values. For example, $^1\Pi$,$^1\Pi$, or $^3\Delta_1$,$^3\Delta_1$, or any transition between two case c states with $\Omega=1$, is like $^3\Pi_1$,$^3\Pi_1$.

theory supported by considerable experimental evidence), the $^3\Pi_0$ levels ($\Omega=0$) show a doubling which exists even for $J=0$ and remains constant with increasing J; the $^3\Pi_1$ levels show a doubling proportional to $J(J+1)$, just like $^1\Pi$ levels; and the $^3\Pi_2$ levels show an extremely small doubling approximately proportional to $J^2(J+1)^2$, just like $^1\Delta$ levels. These relations hold whether A is positive or negative. For the individual coefficients κ_c, κ_d, δ_c, δ_d, etc. in Eq. (56) we may probably assume:[75]

$$^3\Pi_0,\ \kappa_c \neq \kappa_d,\ \delta_c \sim \delta_d;\quad ^3\Pi_1,\ \kappa_c \sim \kappa_d,\ \delta_c \neq \delta_d;\quad ^3\Pi_2,\ \kappa_c \sim \kappa_d,\ \delta_c \sim \delta_d,\ \mu_c \neq \mu_d.$$

As $|A|$ becomes larger (tendency toward case c) the two components of $^3\Pi_0$ should separate more and more widely and regroup themselves until there are two separate sets of levels which can be considered as belonging to two separate electronic states. If $|A|$ is increased sufficiently, these two states become case c 0^+ and 0^- states (cf. Fig. 23 and section *H*1) and are independent of each other. For moderate $|A|$ values, however, they and the $^3\Pi_1$ and $^3\Pi_2$ states are properly considered as forming a case a multiplet. According to Van Vleck,[71] the separation between the two $^3\Pi_0$ states, so long as it is small compared with $|A|$, should increase, other things being equal, about in proportion to A^2. Examples of $^3\Pi_0$ states where the Λ-type doublets are narrower than the distance between the lowest rotational levels are known in the $^3\Pi$, $^3\Pi$ bands of C_2 and N_2; examples where they are much wider probably exist in the halogen bands[77] where, however, the resulting levels are more nearly case *c* than case *a*.

Going in the reverse direction, toward small $|A|$ values, the Λ-type doublet widths tend to become proportional, for all three levels $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ as these approach one another, to $K(K+1)$ of case *b*.

For other than $^3\Pi$ states, analogous relations may be expected,[75] namely for small A, Λ-type doublet widths approaching proportionality to $[K(K+1)]^{\Lambda}$ as in case *b*, and for large $|A|$, doublet widths proportional to $[J(J+1)]^{\Omega}$, with a proportionality constant decreasing rapidly with increasing Ω.

In case *a* $^2\Pi_{\frac{1}{2}}$ states we have, theoretically and experimentally,[75] $\phi_c(J)-\phi_d(J)=a(J+\frac{1}{2})$, for not too large J values, with the coefficient a approximately proportional to A. For $^2\Pi_{1\frac{1}{2}}$ states the doublet widths become smaller with increasing $|A|$, and are experimentally too small to measure if $|A|$ is fairly large. They are (theoretically) proportional to $(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2})$ when $|A|$ is fairly large (true case *a*).

In case *a* $^2\Pi$ states, and in general in case *a* states with S half-integral, we may assume that Eq. (63) holds. For the coefficients in Eq. (63), the following relations probably hold: $^2\Pi_{\frac{1}{2}}$, $\kappa_c\sim\kappa_d$, $\epsilon_c\sim-\epsilon_d$, with $|\epsilon_c|\sim\frac{1}{2}a$ (this relation has been found experimentally in HgH and similar molecules),[75] $\delta_c\sim\delta_d$; $^2\Pi_{1\frac{1}{2}}$, $\kappa_c\sim\kappa_d$, $\epsilon_c\sim\epsilon_d\sim 0$, $\delta_c\sim\delta_d$, $\eta_c\neq\eta_d$.

The behavior of the Λ-type doublets in $^2\Pi$ states in the passage from case *a* to case *b* is discussed in section *J*5.

H. BANDS OF CASE *c* AND INTERMEDIATE CASES (*a-c*, *b-c*)

1. *Nature of case c. Energy levels, quantum numbers, nomenclature.* Before taking up case *c* bands, it is desirable to enlarge the concept of case *c* given[54,55] in Parts II*a* and II*b*. In Part II*a* the various coupling cases were discussed in terms of a molecular model obtained (for fixed nuclei) from an atomic model by separating the latter's nucleus into two parts. A slight separation of the parts causes only a slight perturbation ("weak electric field" in Fig. 10), corresponding[55] to case *c*. The quantum numbers are L, S, and J^a as in the united atom (cf. p. 114), together with Ω, which is the only distinctive molecular electronic quantum number here. If $L=0$ we get case *b* instead of case *c*. A larger separation of the parts, causing a "strong electric field," gives rise to the characteristically molecular quantum number Λ, also to Σ and Ω if $\Lambda>0$. Only S remains as in the united atom. This is case *a* if $\Lambda>0$, or case *b* if $\Lambda=0$.

In addition to the form of case *c* just mentioned (which we shall refer to as the *"close-nuclei"* case *c*) there is another which results if two atoms, each one having a strong coupling of its L with its S to give a J, form a molecular state with small energy of dissociation D, and large r_e, or even with a larger D and smaller r_e if $|A|$ is extremely large. In this *"far-nuclei"* form of case *c*, the molecule as a whole has no electronic quantum numbers L, J^a, or even

---

[77] R. S. Mulliken, Phys. Rev. **36**, 699–705; **36**, 1440–1450 (1930).

S, but has only Ω. In practise the far-nuclei form of case c should be the usual one. Examples approximating this case appear to exist in certain excited states of the halogen molecules.[77]

The following definition seems to cover both forms of case c: "Case c exists whenever the atomic L, S couplings are strong compared with the effects of the departure of the molecule from atomic conditions."

In case b states, Λ and S are the important electronic quantum numbers. The same is true in case a, but Ω is also important. In case c only Ω is important. Case a and b and singlet states are named Σ, Π, Δ, $\cdots$ according as $\Lambda=0, 1, 2, \cdots$, and are also classified as $^1\Pi$, $^2\Pi$, . . . according to the value of S. The rotational levels of such states show Λ-type doubling whenever $\Lambda>0$.

Case c states must be classified according to their Ω values. Instead of introducing a new set of symbols similar to Σ, Π, Δ, $\cdots$, it has been proposed[77] to call case c electronic states simply 0, 1, 2, $\cdots$, states according as $\Omega=0, 1, 2, \cdots$. The rotational levels of such states should show a doubling, which may properly be called "*Ω-type doubling*" since it occurs whenever $\Omega>0$.

The 0 states of case c are divided into two classes which may be called 0^+ and 0^- states, in analogy to the designations Σ^+ and Σ^- in case b. The 0^+ states have positive rotational levels for $J=0, 2, 4, \cdots$ and negative levels for $J=1, 3, \cdots$, while in 0^- states these relations are reversed (cf. Fig. 23).

The two component rotational levels in Ω-type doubling are here defined as e or f levels in the following way: sets of rotational levels $(+-+-\cdots)$ whose lowest level is positive are for all electronic states called e levels, sets $(-+-+\cdots)$ beginning with a negative level are always called f levels (cf. Table V and Fig. 23).[78] 0^+ and 0^- states are thereby automatically classified as having respectively only e and f levels, and might therefore also be called 0^e and 0^f states. All these relations are analogous to those in ordinary singlet states where, however, we have used c and d instead of e and f. Singlet states might indeed be classified just as well under case c as under case a or b'.

To obtain an expression for the energy of a molecule which is applicable to both the near-nuclei and far-nuclei forms of case c, the discussion on p. 114 of Part IIb needs to be generalized somewhat. (1) For near-nuclei, we have J^{a*} giving M as its projection on the electric axis. For $|M|>0$, we have two levels $+|M|$ and $-|M|$ whose energy is equal if the nuclei are held fixed (cf. p. 93 of Part IIb). To this degenerate pair we assign the quantum number $\Omega=|M|$. For $M=0$, there is only one level, with $\Omega=0$. When the molecule rotates, the resulting distortion of the electron system gives rise

---

[78] One might attempt, by means of adiabatic correlations between rotational levels of case c and of cases a and b, to extend the Λ-type doublet designations (c and d) of cases a and b to case c. This, however, leads to conflicting or at least confusing results, so that it seems best to adopt new designations (e and f) for Ω-type doubling. If one wishes, it is possible to use the case c designations e and f also in case a.

to a correction term $\phi(J)$ for exactly the same reasons that give us $\phi(K)$ in singlet states. For $\Omega > 0$, $\phi(J)$ has two forms $\phi_c(J)$ and $\phi_d(J)$ for the same reasons that $\phi(K)$ has two forms in singlet states, and we have Ω-type doubling. (2) For far-nuclei, the J's (J_1 and J_2) of each of two atoms give an M_1 and an M_2. The algebraic sum of M_1 and M_2 is M. When $|M| > 0$, there is for every positive M a corresponding negative M. We then have $\Omega = |M|$, with Ω-type doubling. When $M_1 = M_2 = 0$, we have a single level $\Omega = 0$. When $M_1 = -M_2$, we get two levels 0^+ and 0^-. These arise from a quantum mechanical resonance between the two possible combinations $+M_1 - M_2$ and $-M_1 + M_2$. (3) in both forms of case c, **Ω** and **O** combine to give J^* just as in case a (cf. p. 105 of Part IIb), and the energy is given by

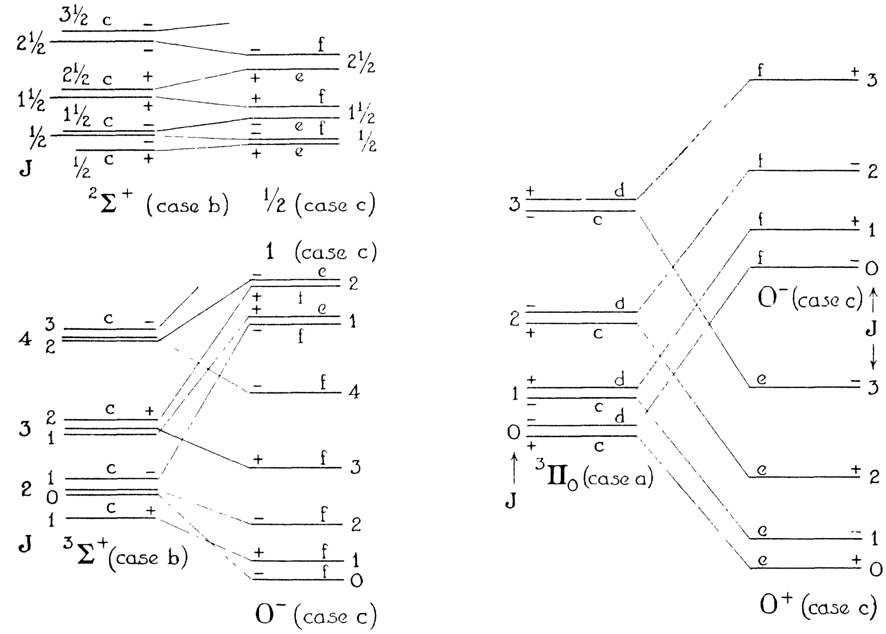


Fig. 23. Rotational energy level diagrams of case a and b states, and of the states into which they go over in case c. The relative spacings of the rotational sub-levels for the different K values in the $^3\Sigma$ state are drawn, assuming $\gamma \rightsquigarrow 0$ in Eq. (33), in accordance with Kramers' formula (cf. equations near middle of p. 107 in Part IIb). Both $^2\Sigma^+$ and $^2\Sigma^-$ (not shown) of case b give $\frac{1}{2}$ states in case c, as do also all case a states (e.g., $^2\Pi_{\frac{1}{2}}$) with $\Omega = \frac{1}{2}$. $^4\Sigma^+$ and $^4\Sigma^-$ would give each a $\frac{1}{2}$ and a $1\frac{1}{2}$ state. $^3\Sigma^+$ states give a 0^- and a 1 state, as shown, while $^3\Sigma^-$ states, as can easily be seen by making appropriate changes in the $^3\Sigma^-$ diagram, give a 0^+ and a 1 state. By suitably redrawing the $^3\Sigma^+$ diagram, it can easily be seen that the results stated would not be changed if the 1 state were below the 0 state in case c. $^5\Sigma^+$ states give a 0^+, a 1, and a 2 state, $^5\Sigma^-$ a 0^-, a 1, and a 2 state. $^3\Pi_0$ states (likewise $^5\Pi_0$, $^5\Delta_0$, etc. states) of case a all give a 0^+ and a 0^- state in case c. This breaking up of states like $^3\Pi_0$ into two states occurs, however, for large $|A|$ values even in case a, before case c is reached (cf. section $G3$).

$$T = T^e + G(v) + B_v[J(J+1) - \Omega^2 + \overline{H^2}] + \phi_i(J) + D_v J^2(J+1)^2 + \cdots \quad (68)$$

This is the same as Eq. (48) except for changes of notation and the substitution of the more general symbol T^e for the not very useful special expression $F_0^{el}+\frac{1}{2}AJ^a(J^a+1)+\cdots$ which holds for the near-nuclei case.

2. *Band structures in case c.* In case *c* the energy as a function of J is the same to within an additive constant as in case *a* and singlet states (cf. Eqs. 31 and 68). The intensity relations also depend on Ω in exactly the same way as in case *a* and singlet states (Eqs. 53–55). The Ω-type doubling of case *c* should also be like the Λ-type doubling of case *a* states, except that doubling should be absent when $\Omega=0$, instead of when $\Lambda=0$.

From the foregoing, we see that case *c* bands with given Ω' and Ω'' must nearly always be just like case *a* or singlet bands with the same Ω' and Ω''. For example, case *c* 0,0 transitions (where the 0's refer to Ω', Ω'') should be just like ${}^1\Sigma,{}^1\Sigma$ transitions; 1, 1 transitions should be like ${}^1\Pi,{}^1\Pi$ and case *a* ${}^3\Pi_1,{}^3\Pi_1$; 1, 0 like ${}^1\Pi,{}^1\Sigma$; $\frac{1}{2}$, $\frac{1}{2}$ like case *a* ${}^2\Pi_{\frac{1}{2}},{}^2\Pi_{\frac{1}{2}}$; $1\frac{1}{2},1\frac{1}{2}$ like case *a* ${}^2\Pi_{1\frac{1}{2}},{}^2\Pi_{1\frac{1}{2}}$; and so on (cf. Figs. 17–19 and 22).

Case *c* 0,0 transitions are of two kinds, $0^+,0^+$ and $0^-,0^-$; $0^+,0^-$ and $0^-,0^+$ transitions are impossible in case *c* for the same reasons that ${}^1\Sigma^+,{}^1\Sigma^-$ and ${}^1\Sigma^-,{}^1\Sigma^+$ are ruled out.[69] The diagrams for ${}^1\Sigma^+,{}^1\Sigma^+$ and ${}^1\Sigma^-,{}^1\Sigma^-$ transitions (Fig. 17) also apply to $0^+,0^+$ and $0^-,0^-$.

3. *Intermediate cases between b, a, and c.* For a good understanding of any of the coupling cases *b*, *a*, *c*, *d*, it is important to investigate the intermediate cases. This is true because the cases that one meets in practise are nearly always to some extent intermediate even though they can be approximately classified under one of the limiting cases *a*, *b*, *c*, or *d*. Suppose we begin by discussing the cases approximating case *a*.

The energy in case *a*, for a state of specified Ω, can be expressed by the following equation of the same form as Eq. (68) of case *c*:

$$T = T^e + G(v) + B^*[J(J+1) - \Omega^2 + C] + \phi_i(J) + D^*J^2(J+1)^2 + \cdots$$

Case *a* in practise only approximates the following characteristics of ideal case *a*: (1) $T^e=T_0^e+A\Lambda\Sigma$; (2) $G(v)$ is independent of Σ; (3) $B^*=B_v$, $D^*=D_v$, $C=G^2+S^2_{perp}$ (cf. Eq. 31), where C is the same for both doublet components if $S=\frac{1}{2}$, but in general depends on Σ, since $S^2_{perp}=S(S+1)-\Sigma^2$. In ideal case *a*, Λ, S, Σ and Ω are all sharply defined quantum numbers.

The real case *a* lies between case *b*, where A is so small that the coupling of Λ and S is overpowered by the rotation, so that Σ and Ω are not defined, and case *c*, where the coupling of L and S to J^a (near-nuclei) or the couplings of L_1 and S_1 to J_1 and of L_2 and S_2 to J_2 (far-nuclei, with $L_1S_1J_1$ and $L_2S_2J_2$ belonging to the separate atoms) are so strong that Λ, Σ, and (for far-nuclei) even S are not good quantum numbers, although Ω is.[79] In the real case *a*, therefore, none of the quantum numbers Λ, S, Σ, Ω of ideal case *a* are quite sharply defined, so that the functions T^e, $G(v)$, $F(J)$ and the band structures show deviations toward either case *b* or case *c* or even toward both simultaneously.

---

[79] Of course if the rotational energy is very small (small J or large reduced mass μ) we can come close to ideal case *a* for small A values, avoiding the influence of both cases *b* and *c*. We are here assuming, however, that the rotational energy is moderately large, as is usually true in experimental work with band spectra.

The deviations toward case *b* show themselves first in a departure of the B^* values from the true B_v values (cf. Eqs. 46 and 67). The C values also show departures from case *a* (cf. Eqs. 46–47). The B_v's themselves, however, likewise the $G(v)$'s and the $\phi(J)$'s, become more and more nearly the same for different multiplet components as we approach case *b*.

Case *a* states, speaking practically, are states in which neither the case *b* departure of the B^*'s from the B_v's, nor the case *c* departures of the $G(v)$'s, B_v's, etc. from a single value (cf. next paragraph) are too large. When the departures toward case *b* or *c* are large, we speak of "intermediate cases"; intermediate cases between *a* and *b* have been treated in Part II*b* and are further treated in section *J*.

Deviations from ideal case *a* toward case *c* cause the different multiplet components to depart from the equidistant spacing given by $T^e = T_0^e + A\Lambda\Sigma$, and also produce differences in the $U(r)$ functions of the different multiplet components, so that (cf. Eqs. 3, 4, 6 of Part I) $G(v)$ and the coefficients B_v, D_v, etc. differ somewhat for different multiplet components. This can be seen in the following way. If, starting from $r = r_e$ for a good case *a* multiplet state, we follow the $U(r)$ curves of the different multiplet components either toward $r = 0$ or toward $r = \infty$, these different curves approach asymptotes whose separations are determined by energy levels of multiplets of the united atom ($r = 0$) or of the separate atoms ($r = \infty$). These asymptotic separations are practically certain to be different from the separations of the $U(r)$ curves for $r = r_e$. The magnitude of this effect and of the deviations toward case *c* depend of course on the size of the L, S coupling coefficients A of the multiplets of the united atom and separate atoms. It is clear, however, that all case *a* states must pass through case *c* when $r \rightarrow 0$ and when $r \rightarrow \infty$.[80] The relations just discussed are illustrated in Figs. 2 and 3 of Ref. 77.

Departures from cases *a*, *b*, and *c* toward case *d* or *e* (rotational uncoupling of Λ or Ω with increasing J) express themselves in the occurrence of $\phi(J)$'s. These are responsible for the occurrence of B^*'s instead of B_v's.

In the previous paragraphs we have seen how case *a* states go over to case *b* states as $A \rightarrow 0$ or J increases, and into case *c* states as $r \rightarrow 0$ or $r \rightarrow \infty$ when $|A|$ is large enough to prevent case *b*. Now let us consider what happens to case *b* states when $r \rightarrow 0$ or $r \rightarrow \infty$. For this purpose we must treat separately case *b* states with $\Lambda > 0$ and those with $\Lambda = 0$. Case *b* states with $\Lambda > 0$ correspond to small $|A|$ values in the molecule and usually also for both united atom and separate atoms. Such states should remain case *b* for practically the entire range of r values. More interesting are the states with $\Lambda = 0$ (Σ states). If these go over as $r \rightarrow 0$ or $r \rightarrow \infty$ into atomic states with $L = 0$, or with very small $|A|$ values, then of course we again have case *b* throughout, or practically throughout, the entire range of r values. But in many cases Σ

---

[80] Case *c* occurs when the effect of the forces associated with the electric axis is weak compared with the L, S coupling or couplings ("weak electric field" in Fig. 10 and Part II*a*);[30] case *a* or *b* when these forces are so strong as to break down the L, S couplings ("strong electric field"), or (case *b*) whenever the L's or S's are zero or the couplings between them are very small.

states go over into atomic states with $L>0$, and if $|A|$ is not too small, we get case c for r values near $r=0$ and for large r values.[80] If the $|A|$'s are large enough, we should get appreciable deviations from case b toward case c even for r near r_e.

Fig. 23 shows some typical examples of the way in which the rotational energy levels of case a and case b states go over into those of case c states. In the examples shown, there is a regrouping of the rotational levels, often in such a way that levels (such as $^3\Sigma$ and $^3\Pi_0$) which are classified as belonging to a single electron level in case a or b are divided between two electron levels in case c (but cf. discussion of $^3\Pi_0$ states in section *G*3). (Splittings of this kind have already been discussed, for fixed nuclei and small r, on p. 95 of Part II*a*).

4. *Band structures in intermediate cases.* In intermediate cases between case a or b and case c, changes in the forms of the branches as compared with either of the limiting cases must occur, except in some special kinds of transitions. Approach to case c also tends to break down the case a selection rule $\Delta\Sigma=0$, thus giving rise to new multiplet components (e.g., $^2\Pi_{1\frac{1}{2}}$, $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$, $^2\Pi_{1\frac{1}{2}}$ in addition to the usual $^2\Pi_{\frac{1}{2}}$, $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$, $^2\Pi_{1\frac{1}{2}}$ of case a) and new branches. It also tends to increase the intensity of intersystem transitions ($\Delta S\neq 0$), especially for far-nuclei case c, where the molecule has no quantum number S. A summary of the changes in band structure which occur in going from case b through case a to case c will be found in section *I*8.

In Σ,Σ transitions, the influence of a tendency toward case c should bring in new branches fulfilling the rule $\Delta J=0, \pm 1$ but having $\Delta K=0, \pm 2, \cdots$ and so (cf. Eqs. 69–71) forbidden in case b (or, strictly speaking, in case b'). It should also make possible ($\Delta J=0, \pm 1, \Delta K=0, \pm 2, \cdots$) some transitions between Σ^+ and Σ^- states, although all such transitions are strictly ruled out in case b.[69] Again, deviations from case c toward case a or b make combinations possible (Q branches only, however) between 0^+ and 0^- states, although these are strictly ruled out in case c.[69] In some other cases too, new branches are to be expected in intermediate coupling cases which are not possible in the limiting cases.

I. CASE *b* MULTIPLET BANDS

1. *Relation of case b multiplet bands to case b′ and singlet bands.* When in an electron state with $S>0$ the total energy is independent of the relative orientation of S and K we have case b' (cf. Part II*b*, p. 108). The band structures corresponding to quantum jumps between two case b' singlet states ($S=0$) have already been discussed (cf. sections E and F and Figs. 17–19). Those for case b' multiplet states ($S>0$) are exactly the same. In *case b* multiplet states (cf. Part II*b*, p. 106), each case b' rotational level of given K and given + or − and c or d character is split into a narrow group of $2S+1$ levels differing in J, but all having the original + or − and c or d character. Similarly in the spectrum arising from a transition between two case b electron states, each band line (K', K'') of case b' is replaced by a narrow group of lines (several values of J', J'' limited by the selection rule

$\Delta J=0, \pm 1$). If we add the intensities of all the components for each such multiple line, the intensity relations among the resulting intensity sums are exactly the same as the intensity relations (Eqs. 53–55) among the undivided lines of case b', provided the distribution factor R in Eq. (53*a*) or (53*b*) is the same for all J values associated with a given K value, as is normally to be expected.

These various relations can be understood from the examples shown in Figs. 24–27. In Fig. 24 the energy levels, and the band lines and their intensities, are compared, for ${}^2\Sigma^+,{}^2\Sigma^+$ case b transitions, with the energy levels and band lines of a case b' Σ^+,Σ^+ transition. (For the corresponding Σ^-,Σ^- transitions, one needs merely to change every $+$ sign in Fig. 24 to a $-$ sign, and vice versa.) In Fig. 25 a similar comparison is made between a case b ${}^2\Pi,{}^2\Sigma^+$ and a case b' Π,Σ^+ transition. The nearly case b ${}^2\Delta,{}^2\Pi$ transition shown in Figs. 26 and 27 should be compared with the ${}^1\Delta,{}^1\Pi$ transition in Fig. 17.

2. *Notation for band lines in case b.* In Part II*b* (pp. 112–13), a classification of case b levels as F_1, F_2, $\cdots$ according as $J=K+S$, $K+S-1$, $\cdots$ has been given. It is often more convenient to speak of T_1, T_2, etc., if we wish to refer to the complete terms instead of just to the rotational part F. In transitions between two case b electron states, the band lines can be designated in a similar manner, by appending numerical subscripts to the designation P, Q, or R which gives the values of ΔJ. The way in which these subscripts are used can be seen from some examples.

$$\begin{aligned}
P_1(J) &= T_1'(J-1) - T_1''(J)\\
P_2(J) &= T_2'(J-1) - T_2''(J)\\
{}^QP_{21}(J) &= T_2'(J-1) - T_1''(J)\\
Q_1(J) &= T_1'(J) - T_1''(J)\\
{}^QR_{12}(J) &= T_1'(J+1) - T_2''(J)\\
{}^RQ_{21}(J) &= T_2'(J) - T_1''(J).
\end{aligned}$$

The first numerical subscript refers to T', the second to T''. When T' and T'' have the same subscript, only one subscript needs to be used after the symbol P, Q, or R. The superscript at the left gives ΔK, which is important in that it determines the *form* of the branch. For instance, ${}^QR_{12}$ is of practically the same form as Q_1 and Q_2, and falls together with these in case b', although it is technically classed as an R branch. The superscript is really implicit in the main symbol and the subscripts, and so can be omitted, but it is often helpful to use it in order to make the classification of the branches more obvious. Not all the combinations P_{21}, R_{12}, Q_{21}, etc. occur in every type of band.

In a similar way, subscripts are used to indicate, just as in singlet and case a bands (cf. Fig. 17), which levels (c or d) in Λ-type doubling are involved in any band line. (For definitions of c and d levels, cf. Table V.) Examples:

$$ {}^{Q}P_{2c1d}(J) = T_{2c}'(J-1) - T_{1d}''(J);\; R_{1c}(J) = T_{1c}'(J+1) - T_{1c}''(J). $$

The allowable combinations of the subscripts c and d differ in the different branches and in different kinds of electron transitions, as in case a and

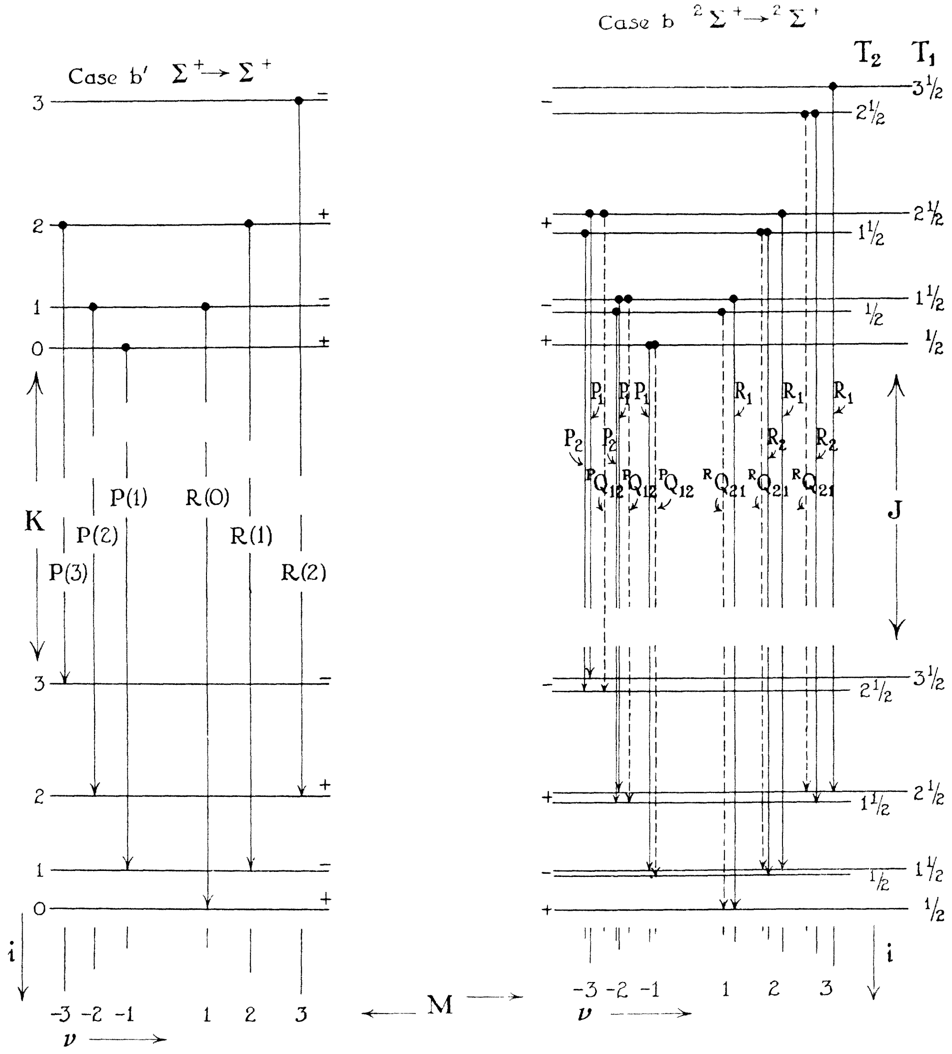


Fig. 24. Lowest rotational levels, and first few lines of each branch with their intensity factors i (cf. Eqs. 53, 70, 71), shown graphically, for a case b' Σ^+,Σ^+ (cf. Fig. 2 of Part I) and a case b ${}^2\Sigma^+,{}^2\Sigma^+$ transition. The satellite branches ($\Delta J \neq \Delta K$) in the ${}^2\Sigma,{}^2\Sigma$ are shown with dashed lines. The spacings of the levels are drawn in accordance with the following relation (cf. Eqs. 32 and 33 of pp. 106–7 of Part IIb with $\Lambda=0$ and $w=0$): $T=Const.+BK(K+1)+\frac{1}{2}\gamma[J(J+1)-K(K+1)-S(S+1)]$, with $\gamma'=0.4B''$, $\gamma''=0.2B''$, and $S=\frac{1}{2}$, for the case b levels, $\gamma=0$ for the case b' levels. $B'=1.1B''$ is assumed in both cases. The order of the sub-levels (T_1 above T_2) in the ${}^2\Sigma$ states is typical, but T_2 above T_1 for one or both is also possible. The rotational levels shown, like those of all Σ^+ states, are all classed as c levels. The M values given under the diagram ($M=-K''$ for $K'=K''-1$ and $M=K''+1$ for $K'=K''+1$) help to make clear the relation of the case b lines to those of case b'.

singlet bands, but can always be readily determined by means of the $+\rightleftarrows-$ selection rule.

3. $^2\Sigma,^2\Sigma$ *bands.* The way in which the positions of the band lines in case *b* differ from those of the corresponding single lines of case *b′* depends on

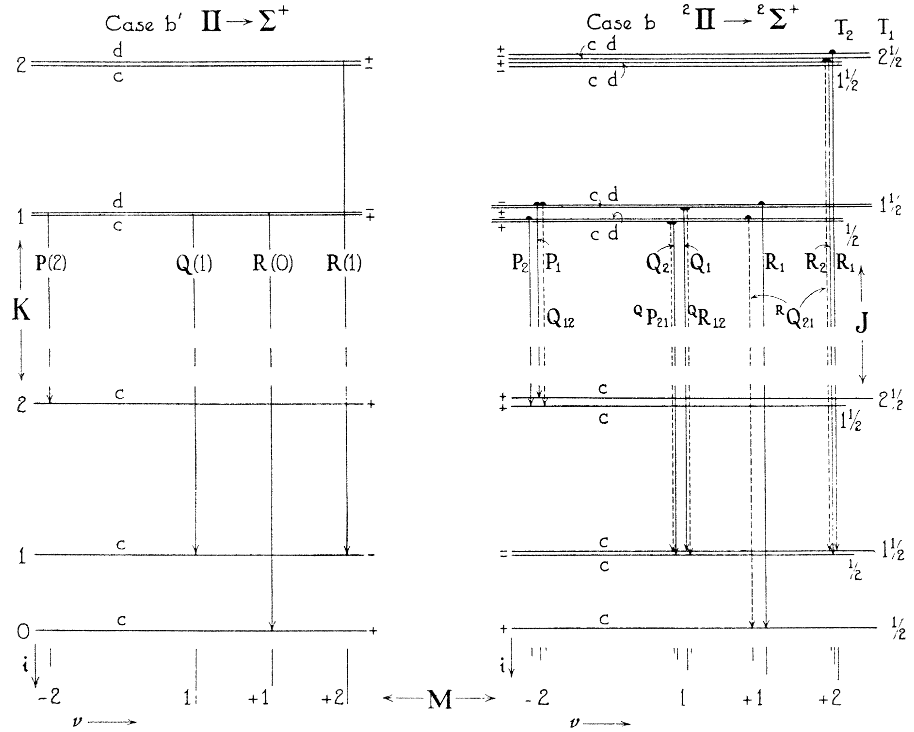


Fig. 25. Lowest rotational levels, and first one or two lines of each branch, with their intensity factors *i* (cf. Eqs. 53, 72, 73) shown graphically for a case *b′* Π,Σ^+ transition and for a case *b* $^2\Pi,^2\Sigma^+$ transition. For simplicity, $B'=B''$ is assumed. The main branches ($\Delta J=\Delta K$) are shown with full lines, the satellite branches ($\Delta J\neq\Delta K$) with dashed lines. The case *b′* levels and lines are the same as for $^1\Pi,^1\Sigma^+$ (cf. Figs. 17, 18, 19). The levels of the case *b* $^2\Pi$ state are drawn exactly the same as those of the case *b′* Π state except for the addition of a term $f(K,J\text{-}K)$ as in Eqs. (32)–(33) of Part II*b* to give the spin doubling (T_1 and T_2 levels, i.e. $J=K\pm\frac{1}{2}$). The Λ-type doublet widths for both T_1 and T_2 levels are proportional to $K(K+1)$ and are the same for a given K value as those of the case *b′* Π state. The spin doublet widths in the $^2\Pi$ levels have been drawn corresponding to $A=B/2$ and $\gamma=0$ (also $w=0$, of course) in Eq. (33) of p. 107, Part II*b*.

The way in which the intensities of the band lines for a case *b′* Π,Σ transition are divided among the various component lines in case *b* can be seen, for the first one or two band lines, from the figure. The course of the intensities for higher J values can be read from Eqs. (73), and is also described in the text. The M values given under the diagram ($M=-K''$ in the P, $M=K''$ in the Q, and $M=+K''+1$ in the R branch) help to make clear the relation of the case *b* lines to those of case *b′*.

The figure is in one respect not typical, although also not impossible, for $^2\Pi,^2\Sigma$: usually when A is very small for the $^2\Pi$ state, giving case *b*, $\gamma\backsim 0$ for the $^2\Sigma$ state. Here, however, a large γ has been assumed in order to show the satellite branches more clearly. When $\gamma=0$ for the $^2\Sigma$ state, the satellite lines coincide with corresponding main lines.

the magnitude and sign of the energy splittings of the rotational levels of the initial and final states in a way which can be seen from Figs. 24–27. We can conveniently discuss this question first for the important case of $^2\Sigma, ^2\Sigma$ transitions.

First we may note an important relation which holds for $^2\Sigma$ states: the magnitude of the coefficient γ in the equations (33 and 36, with $\Lambda = 0$, $w = 0$) which govern the doublet separations of the rotational levels is usually roughly proportional to the coupling constant A of a neighboring $^2\Pi$ level of the same molecule.[81] Commonly the T_1 doublet component ($J = K + \frac{1}{2}$) has a higher energy than the T_2 component ($J = K - \frac{1}{2}$), but this rule is not without exceptions.

In $^2\Sigma, ^2\Sigma$ bands, the structure consists theoretically of two series of triple lines, one series corresponding to the P and the other to the R branch of case b' (cf. Fig. 24). The P series is composed of the sub-series P_1, P_2 and $^PQ_{12}$, the R series of R_1, R_2, and $^RQ_{21}$. Except for the lowest values of K, the satellite branches Q_{12} and Q_{21} are, however, of negligible intensity (cf. Eq. 70*c* and fifth paragraph of section *I*3), so that for practical purposes the P and R series are composed of doublets (P_1 and P_2, R_1 and R_2). In each doublet line, the intensities of the two components are practically equal, except for very small K values (cf. Eqs. 70*a*, 70*b*, and fifth paragraph of section *I*3).

If one takes the center of each doublet line, i.e., $\frac{1}{2}P_1(K) + \frac{1}{2}P_2(K)$ or $\frac{1}{2}R_1(K) + \frac{1}{2}R_2(K)$, the equations for these doublet-centers are of practically[82] the same form as Eqs. (50)–(51) and (58) for P and R branches in case b' Σ, Σ transitions. The doublet separations in the band lines are usually differences of the energy-level doublet separations of the upper and lower $^2\Sigma$ states, and are often very small. Either $P_1(K) > P_2(K)$ and $R_1(K) > R_2(K)$ or $P_1(K) < P_2(K)$ and $R_1(K) < R_2(K)$ is possible, depending on the relative magnitudes and signs of the upper and lower energy-level doublets. The doublet widths of corresponding lines in the P and R branches are more or less unequal, for reasons which can readily be seen from the diagram in Fig. 24.

In cases where the doublets are resolved for the smallest K values, their components become noticeably unequal in intensity in such a way that $I(P_1) > I(P_2)$ and $I(R_1) > I(R_2)$. At the same time some of the intensity is diverted to the satellite branches. In the first line in each series there are are only two components, of which one is the Q (satellite) component. In the first line of the P series we have $P_1(1\frac{1}{2})$ and $^PQ_{12}(\frac{1}{2})$ while in that of the R series we have $R_1(\frac{1}{2})$ and $^RQ_{21}(\frac{1}{2})$, with the Q component half as strong as the other in each case (cf. Fig. 24).

$^2\Sigma, ^2\Sigma$ bands have in general two heads (a P_1 and a P_2, or an R_1 and an R_2

---

[81] Cf. J. H. Van Vleck, Phys. Rev. **33**, 497–500 (1929).

[82] If the doublet separations are measurable for small K values, the doublet-*centers* no longer follow Eqs. (50) and (51) exactly, since the energy-level doublet splittings become distinctly unsymmetrical for small K values (cf. Eq. 33 of Part II*b* with $A = 0$, and Fig. 24). If suitable *centers of gravity* are used for each doublet (or rather, triplet), Eqs. (50) and (51) should, however, still hold exactly.

head). These are visibly separated, however, only if the doublet widths are fairly large, as in molecules with large Λ, S coupling (large A in states with $\Lambda > 0$), e.g. HgH.

The intensity relations which have been discussed in the preceding para graphs are expressed quantitatively by the following theoretical equations;[83] these can be obtained as special cases of Eqs. 70–71 by putting $\Lambda' = \Lambda'' = 0$ in the latter:

$$P_1 \text{ or } R_1 \text{ branch: } i = 2K(K+1)/(2K+1) = (J^2 - \tfrac{1}{4})/J \qquad (69a)$$

$$P_2 \text{ or } R_2 \text{ branch: } i = 2K(K-1)/(2K-1) = (J^2 - \tfrac{1}{4})/J \qquad (69b)$$

$$Q_{12} \text{ or } Q_{21} \text{ branch: } i = 2K/(4K^2-1) = (2J+1)/4J(J+1). \qquad (69c)$$

In these equations, K, or J, is the larger of the two quantities K' and K'', or J' and J'', except that in the Q branches $J = J' = J''$. The complete intensity relations are determined by Eqs. (69) in connection with Eqs. (53), which apply exactly as before.

In practise, Eqs. (53c) and (69) usually hold well for ${}^2\Sigma,{}^2\Sigma$ emission bands.[83,84] The predicted approximately symmetrical distribution of the P and R series, with slightly higher intensity of the P series because of the Boltzmann factor in Eq. (53c), is fulfilled. The approximate intensity equality of the doublet-components for large K values, and the inequalities and other relations predicted for low K values, appear usually to be fulfilled.[83,84] There are, however, exceptions. In the C bands of CaH, whose upper level seems to be of an unstable type, one component of each doublet is much weaker than the other or even entirely missing under some conditions.[85] In certain HgH bands,[85] the P_1 and R_2 branches are about two or three times as strong as the P_2 and R_1 branches for all K values. The explanation of these peculiarities is not known. In the case of CaH they can be attributed to unusual excitation behavior reflected in the distribution factor R' in Eq. (53a). In the HgH case, however, even this possible explanation fails.

4. ${}^3\Sigma,{}^3\Sigma$ *and other* Σ,Σ *bands.* Other Σ,Σ transitions should show characteristics similar to those of ${}^2\Sigma,{}^2\Sigma$. In all such transitions, excepting intersystem combinations, the number of *strong* components (main branches) into which the lines of the P and R series of case b' split is $2S+1$. There are also other components (satellites) whose intensity is negligible except for the lowest K values. In ${}^3\Sigma,{}^3\Sigma$ transitions, for example, using the rule $\Delta J = 0, \pm 1$, we see that the P branch of case $b'(K' = K'' - 1)$ should split into P_1, P_2, P_3 (all strong), ${}^PQ_{12}$ and ${}^PQ_{23}$ (very weak), and ${}^PR_{13}$ (exceedingly weak), while the R branch $(K' = K'' + 1)$ should give R_1, R_2, R_3 (strong), ${}^RQ_{32}$ and ${}^RQ_{21}$ (very weak), and ${}^RP_{31}$ (exceedingly weak). The strong branches, as in ${}^2\Sigma,{}^2\Sigma$ transitions, are those in which $\Delta J = \Delta K$. That this must be true can

---

[83] R. S. Mulliken, Phys. Rev. **30**, 138 (1927).

[84] Violet CN bands, F. A. Jenkins, Phys. Rev. **31**, 556 and Fig. 1, *F* (1928). N_2^+ bands, L. S. Ornstein and W. R. Van Wijk, Zeits. f. Physik **49**, 315 (1928).

[85] CaH bands, cf. E. Hulthén, Phys. Rev. **29**, 97 (1927); and another reference (1930). HgH bands, E. Hulthén, Zeits. f. Physik **50**, 332–33 (1928); W. Kapuściński and J. G. Eymers, Zeits. f. Physik **54**, 251 (1929); the subscripts 1 and 2 are reversed in Hulthén's notation.

be seen by an application of the correspondence principle, and also follows from the quantitative intensity equations (not yet given for this case, but easily derivable).

In $^3\Sigma,^3\Sigma$ transitions, no general rules can be given for the order and spacing of the three components $P_1P_2P_3$ or $R_1R_2R_3$ of a given line of the P or R series. The order of the three levels $J=K$, $K\pm1$ in a $^3\Sigma$ state depends on the sum of two energy functions, usually both small,[86] namely $w(K, J-K)$ and $f(K, J-K)$ of p. 107, Part II*b*. (Cf. Fig. 34 for an example showing actual spacings in a $^3\Sigma$ state.) Since these functions are quite different in form, and both also differ for initial and final states, the possible arrangements of the components of the band lines are numerous. Crossings of component branches with changing K are often to be expected.[87] $^3\Sigma,^3\Sigma$ bands should have in general three heads, visibly separated, however, only if the triplet separations are fairly large. Examples of $^3\Sigma,^3\Sigma$ bands are known in O_2, S_2, and SO.[55a,87]

No $^4\Sigma,^4\Sigma$ bands or Σ,Σ bands of higher multiplicity are yet known.

5. *Other case b bands.* The band structures for transitions between *any two case b* states are always related to those for the corresponding case *b′* or singlet states in the manner already discussed for $^2\Sigma,^2\Sigma$ and $^3\Sigma,^3\Sigma$ bands. Each line of the case *b′* band is replaced by a group of $2S+1$ strong components for which $\Delta J=\Delta K$, together with additional weak components for which $\Delta J=0,\pm1$, but $\Delta J\neq\Delta K$. The strong components corresponding to a given case *b′* line are practically equal to one another in intensity except for very small K values. The weak components are of altogether negligible intensity except for the very lowest K values.

Fig. 25, which with its caption is largely self-explanatory, shows the band structure and intensity relations for a typical case $b\ ^2\Pi\rightarrow^2\Sigma$ transition.[90] It also shows well the arrangement of the rotational levels for a typical case $b\ ^2\Pi$ state with $A>0$ (in the figure, $A=B/2$ is assumed). In a case $b\ ^2\Pi,^2\Sigma$ transition, we have for large K values the branches Q_1, Q_2 (about equally strong), R_1, R_2, P_1 and P_2 (each about half as strong as each Q branch). For low K values, the R branches gain in intensity at the expense of the P branches, just as in a $^1\Pi,^1\Sigma$ transition (cf. Fig. 18). For the lowest K values the satellite branches take on appreciable intensity. The R and P branches each have one satellite, namely $^RQ_{21}$ and $^PQ_{12}$ respectively, while the Q branches have two satellites, $^QP_{21}$ and $^QR_{12}$. Some equations for doublet separations applicable to case *b* bands will be found in section *J*. Of these only Eq. (85) is of much interest, since the others (Eqs. 77, 85*a*, 85*b*) involve the very weak satellite branches.

Diagrams similar to Fig. 25 can readily be constructed in an analogous manner for other case *b* transitions. Figs. 26–27 show a (nearly) case *b* $^2\Delta,^2\Pi$ transition. Fig. 31 shows the possible main and satellite branches (full

---

[86] The magnitude of f, as in the case of $^2\Sigma$ states, should become larger for heavy molecules, increasing approximately in proportion to the A values of their $^3\Pi$ states.

[87] For further details in regard to an actual example, cf. W. Lochte-Holtgreven and G. H. Dieke, Ann. der Physik [5], 3, 937 (1929): O_2 bands.

and dashed lines) for a $^3\Pi,^3\Sigma$ transition in case *b*. It also shows additional transitions (dotted lines) which are expected for $^3\Pi,^3\Sigma$ with case *a* $^3\Pi$, but these can be disregarded for present purposes.

When Λ' and Λ'' are both greater than zero, there are twelve main branches and eight satellite branches. The latter are of negligible intensity except for very low J values. As an example, the $^2\Delta,^2\Pi$ CH band near λ4300 may be cited (Figs. 26 and 27).[88] Here, to be sure, the $^2\Pi$ energy levels for the lowest J values show a considerable departure from case *b* toward case *a*, but the $^2\Delta$ energy levels, and the intensity relations in the bands, are good case *b* for all J values. Fig. 26 shows the energy levels and the transitions for the lowest values of J, while Fig. 27 shows by means of a Fortrat diagram how the band lines are arranged. A discussion of further relations in this band will be found in section *J4a*.

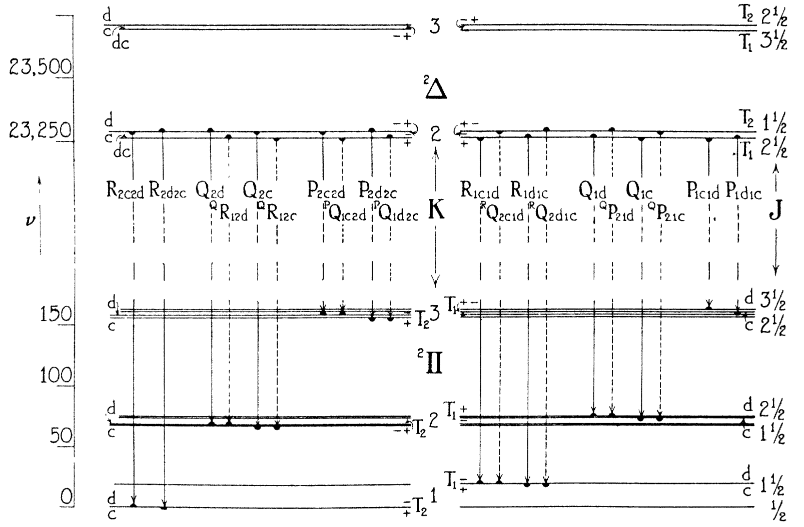


Fig. 26. Lowest rotational levels, and first line of each branch, for the $^2\Delta,^2\Pi$ band of CH at λ4300. The full lines correspond to main branches, the dashed lines to satellite branches. The rotational levels are all drawn to scale (cf. R. S. Mulliken, Phys. Rev., **30**, 797, 1927), except that *the Λ-type doublet separations in the* $^2\Pi$ *levels, and the spin doublets* (T_1, T_2) *in the* $^2\Delta$ *levels, are exaggerated threefold.* The Λ-type doublets of the $^2\Delta$ levels are so small that they have not been detected experimentally. The $^2\Delta$ state is good case *b* with $A \backsim -1, B = 14.57$, while the $^2\Pi$ state has $B = 14.19$ and $A/B = +2.0$ and is of a type intermediate between cases *a* and *b* for the low J values, but is good case *b* for high J values. The intensity relations found in this band (not shown here) are essentially those of case *b*. The + and − labelling of the levels is based on data on the λ3900 band of CH, assuming this to be a $^2\Sigma^-,^2\Pi$ transition (cf. T. Hori, Ref. 91).

6. *Intensity relations in case b.* The following equations, taken in connection with Eqs. (53), give quantitatively the theoretically expected intensity relations[88] for transitions between any two case *b doublet* states ($S = \frac{1}{2}$):

---

[88] For derivation of case *b* intensity relations, cf. R. S. Mulliken, Phys. Rev. **30**, 787–88 (1927); or Ruark and Urey, Atoms, Molecules, and Quanta, p. 718 (McGraw Hill, 1930).

$$\Lambda' = \Lambda'',\ K' = K'',\ Q_1:\ i = 2\Lambda^2(2K+3)/(K+1)(2K+1) \quad (70a)$$

$$Q_2:\ i = 2\Lambda^2(2K-1)/K(2K+1) \quad (70b)$$

$$^QP_{21} \text{ and } ^QR_{12}:\ i = 2\Lambda^2/K(K+1)(2K+1) \quad (70c)$$

$$\Lambda' = \Lambda'',\ K' = K'' \pm 1,\ P_1 \text{ and } R_1:\ i = 2(K+1)(K^2-\Lambda^2)/K(2K+1) \quad (71a)$$

$$P_2 \text{ and } R_2:\ i = 2(K-1)(K^2-\Lambda^2)/K(2K-1) \quad (71b)$$

$$^PQ_{12} \text{ and } ^RQ_{21}:\ i = 2(K^2-\Lambda^2)/K(4K^2-1) \quad (71c)$$

$\Lambda' = \Lambda'' \pm 1,\ K' = K''$,

$$Q_1:\ i = (K+\Lambda)(K-\Lambda+1)(2K+3)/(K+1)(2K+1) \quad (72a)$$

$$Q_2:\ i = (K+\Lambda)(K-\Lambda+1)(2K-1)/K(2K+1) \quad (72b)$$

$$^QP_{21} \text{ and } ^QR_{12}:\ i = (K+\Lambda)(K-\Lambda+1)/K(K+1)(2K+1) \quad (72c)$$

$\Lambda' = \Lambda'' \pm 1,\ K' - K'' = \Lambda' - \Lambda''$,

$$R_1 \text{ or } P_1:\ i = (K+\Lambda)(K+\Lambda-1)/K(2K+1) \quad (73a)$$

$$R_2 \text{ or } P_2:\ i = (K+\Lambda)(K+\Lambda-1)/K(2K-1) \quad (73b)$$

$$^RQ_{21} \text{ or } ^PQ_{12}:\ i = (K+\Lambda)(K+\Lambda-1)/K(4K^2-1) \quad (73c)$$

$\Lambda' = \Lambda'' \pm 1,\ K' - K'' = \Lambda'' - \Lambda'$,

$$P_1 \text{ or } R_1:\ i = (K-\Lambda)(K-\Lambda+1)(K+1)/K(2K+1) \quad (74a)$$

$$P_2 \text{ or } R_2:\ i = (K-\Lambda)(K-\Lambda+1)(K-1)/K(2K-1) \quad (74b)$$

$$^PQ_{12} \text{ or } ^RQ_{21}:\ i = (K-\Lambda)(K-\Lambda+1)/K(4K^2-1) \quad (74c)$$

In these i equations, K is always the larger of the two quantities K' and K'', Λ the larger of the quantities Λ' and Λ''. Eq. (73*a*) applies to R_1 if $\Lambda' = \Lambda''+1$, to P_1 if $\Lambda' = \Lambda''-1$, and Eqs. (73*b*) – (74*c*) involve similar alternatives. When Λ' and Λ'' are both greater than zero, each band-line given by the above equations shows Λ-type doubling, and the intensity given by Eqs. (53) and (70)–(74) is divided equally between the two components unless the excitation function R of Eqs. (53) is of an abnormal kind.

7. *Λ-type doubling in case b.* In the case b $^2\Pi$ state of Fig. 25, the Λ-type doublet widths have been drawn proportional to $K(K+1)$, and of the same width for $J = K \pm \frac{1}{2}$. Experimentally and theoretically, these relations are correct. When S is loosely coupled to Λ as in case b, the Λ-type doublets are practically the same as if S were not coupled at all, or as if $S=0$. If the coupling of S to Λ is increased, however (transition toward case a), the Λ-type doublet widths become increasingly different for $J = K+\frac{1}{2}$ and $J = K-\frac{1}{2}$ (cf. sections $G3$ and $J5$).

A good example of typical case b Λ-type doublet relations is found in the $^2\Delta, ^2\Pi$ band of CH (cf. Figs. 26, 27), in spite of the fact that the $^2\Pi$ state tends toward case a for the lowest J values. The Λ-type doublet widths in the $^2\Pi$ state are given approximately by $0.036K(K+1)$ for both $J = K+\frac{1}{2}$ and $J = K-\frac{1}{2}$ (the separations are at first slightly larger for the T_2 than for the T_1 levels, but become equal for larger K values). In the $^2\Delta$ state the Λ-type doublet widths are practically zero, for both $J=K+\frac{1}{2}$ and $J=K-\frac{1}{2}$, just as the theory demands for a $^1\Delta$ state (cf. section $G3$). The way in which the Λ-type doubling appears in the band-lines can be seen from Fig. 27, and is further discussed in section J.

8. *Comparison of band structures in cases b', b, a, c.* If we think first of a case b', then of a case b, then of a case a transition, all with the same values of S, Λ' and Λ'', and consider finally the same transition in case c, we have first

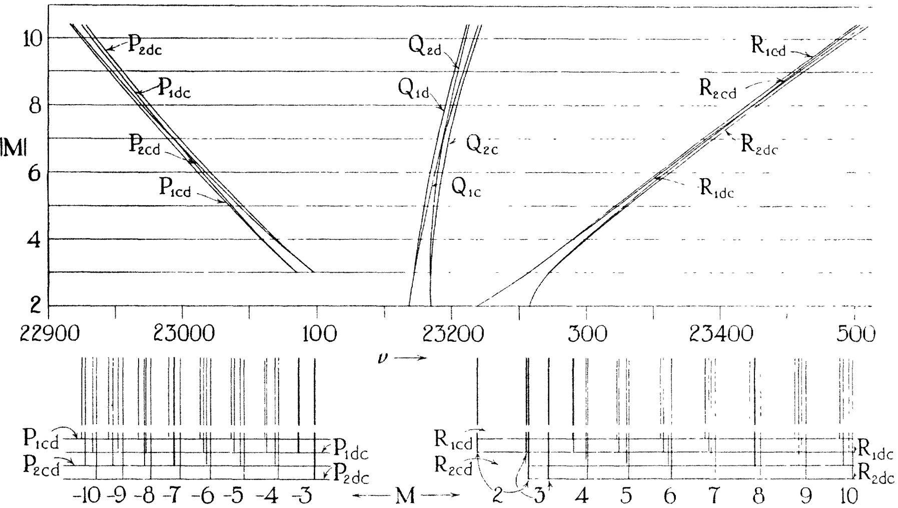


Fig. 27. Fortrat diagram of *main branches* of CH λ4300 band (cf. Fig. 26). The data are from E. Hulthén, Dissertation Lund, 1923; cf. also R. S. Mulliken, Phys. Rev. **30**, 801 (1927). The intensity relations (not shown here) are essentially those of case b. It will be noted that there are four main P, four main Q, and four main R branches. For a given value of K or $M(M=-K''$ in the P, $M=K''$ in the Q, and $M=+K''+1$ in the R branches), corresponding lines of the four P branches form a close group. In order that *the spacings of the lines in such a group*, and their variation with M, shall be clearly visible, they *have all been exaggerated two-fold* both in the Fortrat curves above and in the ν diagram below. The same has been done in the Q and R branches. This should be borne in mind if one wishes a true picture of the band.

In the part of the diagram showing the actual arrangement (*except as above noted*) of band lines in the spectrum, the Q branches are omitted because they are too crowded to show to advantage. In the P and R branches, one has for the lowest $|M|$ values rather wide doublets P_1 and P_2, R_1 and R_2, due to the spin. These, however, contract rapidly with increasing $|M|$ (transition from case a to case b). At the same time each component, e.g., P_1, splits into two (P_{1c} and P_{1d}), as a result of Λ-type doubling, giving quadruple lines. The Λ-type doublet widths increase rapidly with $|M|$. For large $|M|$ values the spin doubling becomes almost imperceptible, so that we now have again practically only doublets, e.g. P_c and P_d. These changes can be readily followed and understood from the Fortrat diagram.

in case b' a single band with single lines, then in case b a single band each line of which is split into a narrow group of components, $2S+1$ in number if we neglect weak satellites and leave the lowest K values out of consideration, then in case a first a division of each band into a group of $2S+1$ sub-bands, changing for larger A values into a division of the band system into $2S+1$

sub-systems, which in case *c* become entirely separate. Reference should be made to Sections *H*3 and *H*4, and to section *J*, for a more detailed treatment of intermediate cases.

J. MULTIPLET BANDS, INTERMEDIATE AND MIXED CASES BETWEEN *a* AND *b*

1. *Introduction.*—In many band spectra there is case *a* coupling in the initial state, case *b* coupling in the final state, or vice versa (*"mixed case"*). Important types are: $^2\Pi$(case *a*)$\rightarrow ^2\Sigma$ and $^2\Sigma \rightarrow ^2\Pi$(case *a*), $^2\Delta$(case *b*)$\rightarrow$ $^2\Pi$(case *a*), $^3\Pi$(case *a*)$\rightarrow ^3\Sigma$. Another frequently occurring possibility is that one state is case *b* or case *a*, while the other is intermediate between *a* and *b*; or both states may be intermediate between cases *a* and *b* (*"intermediate cases"*). Hill and Van Vleck have shown[89] how the theoretical intensity equations of the band lines can be obtained, when $S = \frac{1}{2}$, for both intermediate and mixed cases.

In such bands, equations for the branches as functions of the quantum numbers often have complicated forms. These can, of course, always be obtained by taking $T' - T''$, using suitable term equations (cf. Part II*b*, pp. 108–13), but usually this is not worth while. In the following paragraphs, explicit equations will be given only for the important case of $^2\Pi, ^2\Sigma$ transitions with a case *a* $^2\Pi$ state.

In bands of the kind now under discussion, the only strict selection rules are those which are common to case *a*→case *a* and to case *b*→case *b* transitions. These are: for the electronic state, $\Delta\Lambda = 0, \pm 1$; for the rotational levels, $\Delta J = 0, \pm 1$, and positive $\rightleftarrows$ negative.

In the special intermediate case that both initial and final states are at about the same intermediate stage between cases a and *b*, the qualitative intensity relations can easily be obtained by interpolating between those which hold for case *a*→case *a* and for *b*→*b* transitions. In a $^2\Pi \rightarrow ^2\Pi$ transition, for example, we have, if both states are case *a*, two *P*, two weak *Q*, and two *R* branches, each with Λ-type doubling. If both states are case *b*, we have exactly the same branches, although their arrangement is different, but in addition have four very weak (satellite) branches with Λ-type doubling. By interpolation, intermediate cases here have practically the same intensity relations as both limiting cases. But if one $^2\Pi$ state were case *a* or nearly case *a* and the other case *b* or nearly case *b*, such an interpolation would not be applicable. In fact the intensity relations for such a mixed case are very different than for the kind of intermediate case just discussed. In section *J*4*b* an example of a "mixed case" and of an "intermediate case" $^2\Pi, ^2\Pi$ transition are cited.

In practise, the most numerous examples of transitions of mixed and inter-

---

[89] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 263–67 (1928). For equations for $^2\Pi$(case *a*),$^2\Sigma$, cf. p. 266. On p. 33 of Ruedy's book (*l. c.* Ref. 59), Hill and Van Vleck's equations are given with P_2 and P_{21} where P_{12} and P_1 should be, and vice versa, also Q_2 and Q_{21} for Q_{12} and Q_1, and R_2 and R_{21} for R_{12} and R_1.

mediate type are found in $^2\Pi,^2\Sigma$ and $^2\Sigma,^2\Pi$ bands,[90,91] and the following treatment will deal mainly with these. The structure and intensity relations in such bands are primarily a function of A/B of the $^2\Pi$ state, whose magnitude determines the extent to which this state approaches case *a* or *b*. No corresponding variation in the character of the $^2\Sigma$ states needs to be considered, since except for possible tendencies toward case *c* or *d*, $^2\Sigma$ levels are always case *b*. We must, however, consider the effect of the doublet widths of the $^2\Sigma$ levels on the band structure, and must also not forget that there is a difference between Σ^+ and Σ^- states in respect to the selection rules for their combination with *c* and *d* rotational levels of $^2\Pi$ states (cf. last paragraph of section *J*2).

2. $^2\Pi,^2\Sigma$ *and* $^2\Sigma,^2\Pi$ *bands with case a* $^2\Pi$ *state.* It will be convenient to begin with the extreme case (mixed case) of a definitely case *a* $^2\Pi$ state (large $|A|/B$). The other extreme case (small $|A|/B$, case *b* $^2\Pi$ as well as $^2\Sigma$ state) has already been treated (cf. Fig. 25 and section *I*5). Intermediate cases will then be considered with reference to these two extremes.

We shall begin with equations for the band lines. First we need expressions for the term-forms. Neglecting terms in powers of J higher than J^2, these are[92]

$$^2\Pi_{\frac{1}{2}}\colon\ T_{1c}(J) = W_1 + \tfrac{1}{2}a(J+\tfrac{1}{2}) + B_1J(J+1) + \cdots \tag{75a}$$

$$T_{1d}(J) = W_1 - \tfrac{1}{2}a(J+\tfrac{1}{2}) + B_1J(J+1) + \cdots \tag{75b}$$

$$^2\Pi_{1\frac{1}{2}}\colon\ T_{2c}(J) = T_{2d}(J) = W_2 + B_2J(J+1) + \cdots \tag{75c}$$

$$\begin{aligned} ^2\Sigma,\ J = K+\tfrac{1}{2}\colon\ T_1(J) &= W + \tfrac{1}{2}\gamma K + BK(K+1) + \cdots \\ &= W + \tfrac{1}{2}\gamma(J-\tfrac{1}{2}) + B(J-\tfrac{1}{2})(J+\tfrac{1}{2}) + \cdots \end{aligned} \tag{75d}$$

$$\begin{aligned} ^2\Sigma,\ J = K-\tfrac{1}{2}\colon\ T_2(J) &= W - \tfrac{1}{2}\gamma(K+1) + BK(K+1) + \cdots \\ &= W - \tfrac{1}{2}\gamma(J+1\tfrac{1}{2}) + B(J+\tfrac{1}{2})(J+1\tfrac{1}{2}) + \cdots \end{aligned} \tag{75e}$$

Eqs. (75*a*)-(75*c*) are equally valid for $A>0$ (regular $^2\Pi$ states) and for $A<0$ (inverted $^2\Pi$). In the equations for the $^2\Pi$ states, B_1 stands for $B_1^*+\delta$ (cf. Eq. 46 of Part II*b* for B^*), B_2 for $B_2^*+\delta$,

---

[90] Cf. R. S. Mulliken, Phys. Rev. **32,** 388 and 997 (1928), and Ref. 59, for detailed analysis of examples of $^2\Pi$, $^2\Sigma$ and $^2\Sigma$, $^2\Pi$ bands; also W. W. Watson, Phys. Rev. **32,** 600, 1928 and **37,** 167, 1931 (BeH); W. W. Watson and W. Bender, Phys. Rev. **35,** 1513, 1930 (CaH); E. Svensson, Zeits. f. Physik **59,** 533, 1930 (CdH); G. M. Almy, Phys. Rev. **35,** 1495, 1930 (OH). For a review of experimentally observed intensity relations, cf. p. 393 of the writer's paper.

[91] Analysis of CH λ3900 and λ4300, cf. R. S. Mulliken, *l. c.* Ref. 88. Analysis of CH λ3900 and λ3143, cf. T. Hori, Zeits. f. Physik **59,** 918 (1929).

[92] In obtaining these equations, we assume $\phi_c(J)=\frac{1}{2}a(J+\frac{1}{2})+\delta J(J+1)+\cdots$, $\phi_d(J)=-\frac{1}{2}a(J+\frac{1}{2})+\delta J(J+1)+\cdots$, for the $^2\Pi_{\frac{1}{2}}$ state (cf. Eq. 63 and section *G*3), and $\phi_c(J)=\phi_d(J)=\delta J(J+1)+\cdots$ for the $^2\Pi_{1\frac{1}{2}}$ state (cf. section *G*3); δ is assumed to have practically the same value for the *c* as for the *d* rotational levels, and for $^2\Pi_{1\frac{1}{2}}$ as for $^2\Pi_{\frac{1}{2}}$. For the $^2\Sigma$ levels, we are using Eq. (32) of Part II*b* with $\Lambda=0$ and $\phi(K,J)$ set equal to $\delta K(K+1)+\cdots$ (cf. section *F*2 and Eqs. 56–58 which, with K in place of J, apply to case *b* states as well as to case *b*′ singlet states), where the value of δ is in general different from that of δ of the $^2\Pi$ states.

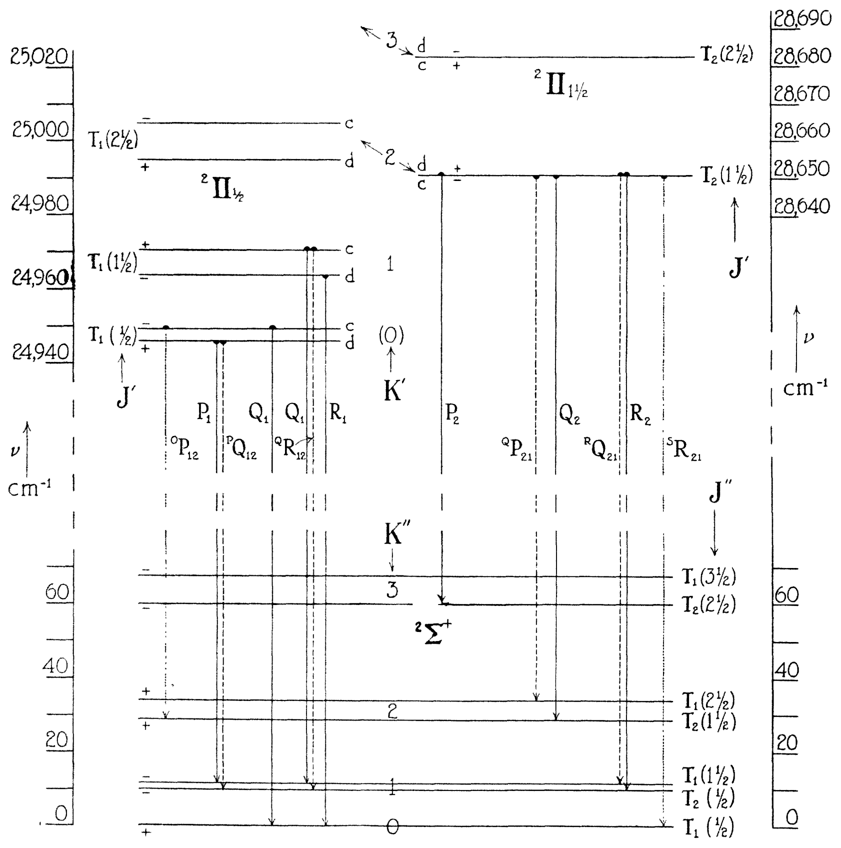


Fig. 28. Lowest rotational energy levels and lowest quantum number transitions in the $^2\Pi\rightarrow{}^2\Sigma^+$ bands of HgH with $v'=0$, $v''=0$. In these bands B_1, B_2, B, a, and γ of Eqs. (75) and (76) have the respective values 6.56, 6.61, 5.39, 3.40, and 2.10 (cf. E. Hulthén, Zeits. f. Physik 50, 334, 1928). The intervals between the $^2\Sigma$, the $^2\Pi_{\frac{1}{2}}$ and the $^2\Pi_{1\frac{1}{2}}$ states are so large that they cannot be drawn to scale in the diagram, but they are indicated by the ν scales at left and right. The designations c and d, T_1 and T_2, have been assigned by means of a correlation of the levels with those of case b (cf. Table V, Ref. 58, and Fig. 16). The notation used for the lines likewise corresponds to case b (cf. section *12*).

The so-called K' values for the $^2\Pi$ state are virtual values of K' obtained from the J values according to the definitions $K'=J'-\frac{1}{2}$ for $^2\Pi_{1\frac{1}{2}}(T_1)$ and $K'=J'+\frac{1}{2}$ for $^2\Pi_{\frac{1}{2}}(T_2)$, i.e. they are the K values which the levels would take on if we could make $A\rightarrow 0$. The lowest level, $J=\frac{1}{2}$, of $^2\Pi_{\frac{1}{2}}$, is assigned to $K'=(0)$, since it is classified as a T_1 level in case a, although really, if we could make $A\rightarrow 0$, $J=\frac{1}{2}$ would become $T_2(\frac{1}{2})$,—cf. Fig. 15—which corresponds to $K'=1$.

In the band line symbol, the main symbol P, Q, or R represents ΔJ, which in the "main branches" (full lines) is equal to ΔK. The superscript symbol P, Q, or R in the "satellite branches" (dashed lines), where $\Delta J\neq\Delta K$, represents ΔK; such branches would in case b be very weak. The superscript symbol O means $K'-K''=-2$, S means $K'-K''=+2$; the branches with these superscripts are shown by dotted lines corresponding to the fact that they would be "forbidden" in case b by the selection rule $\Delta K=0,\pm 1$. With a case a $^2\Pi$ state as here, the branches which in case b would be main, satellite, and forbidden are all strong branches. The distinctions between them are made here, and virtual K values are assigned in the $^2\Pi$ levels, only in order to facilitate comparison with bands having case b $^2\Pi$ levels or $^2\Pi$ levels intermediate between cases a and b (cf. Fig. 30).

The order of the T_1 and T_2 levels in the $^2\Sigma$ state, and of the c and d levels in the $^2\Pi_{\frac{1}{2}}$ state, is that which is usual (cf. Figs. 22 and 24). The separations of the c and d levels are so small in the $^2\Pi_{1\frac{1}{2}}$ states that their order is not certain for low J values (cf. E. Hulthén, *l. c.*) but it is here shown opposite to that in the $^2\Pi_{\frac{1}{2}}$ state, in accordance with Van Vleck's theoretical results (cf. Part II*b*, Fig. 16). The labelling of the rotational levels as + and − is based on the assumption (extremely probable on the basis of a study of possible electron configurations and dissociation products) that the $^2\Sigma$ level is $^2\Sigma^+$.

$$W_1 = T_1{}^e + G_1(v) + C_1 + B_1(\overline{G^2} - \Omega^2 + S^2{}_{perp}) = T_1{}^e + G_1(v) + C_1 + B_1(\overline{G^2} + \tfrac{1}{4}),$$

$$W_2 = T_2{}^e + G_2(v) + C_2 + B_2(\overline{G^2} - \Omega^2 + S^2{}_{perp}) = T_2{}^e + G_2 + C_2 + B_2(G^2 - 1\tfrac{3}{4}),$$

while a is a small constant, usually positive. In the $^2\Sigma$ equations,[92] B stands for $B_v+\delta$, W stands for $T^e+G(v)+B\overline{G^2}$, and γ is a small constant. The quantities B_v, δ, $G(v)$, $\overline{G^2}$, etc. mentioned have of course different values for the $^2\Pi$ and $^2\Sigma$ states. Experimentally and theoretically (cf. sections *G*3 and *I*3) the coefficients α and γ are both approximately proportional to A of the $^2\Pi$ state.

It will be convenient to develop the band-line equations in connection with an energy-level diagram for a typical example. Fig. 28 shows the energy levels and their relation to the possible branches for the $^2\Pi, ^2\Sigma^+$ bands of HgH,[90] which have a case a regular $^2\Pi$ state. As a result of the rotational selection rules $\Delta J = 0, \pm 1$ and $+ \rightleftarrows -$, there are twelve strong branches, namely two P, two Q, and two R branches in each of the two sub-bands corresponding to $^2\Pi_{1\frac{1}{2}}, ^2\Sigma$ and to $^2\Pi_{\frac{1}{2}}, ^2\Sigma$. [Really in the $^2\Pi$ of HgH A is so large that these "sub-bands" are separate bands belonging to two separate subsystems (cf. Fig. 20), with six branches in each such separate band (cf. Fig. 28).]

Before giving the equations for the different branches, an explanation of the notation used here is necessary. This notation is one corresponding to a *case b* $^2\Pi, ^2\Sigma^+$ transition (cf. section *I*2).[93] The reason for using this notation is that it will facilitate comparison between different $^2\Pi, ^2\Sigma$ transitions having $^2\Pi$ states with various intermediate stages of coupling between cases a and b.[94]

With the definitions of the branches which can be read from Fig. 28, substituting according to Eqs. (75) for the terms T, and reducing, we get the following equations (76*a*)–(76*e*).[95] The equations are here given, contrary to the conventional practise, in terms of J', because this form will prove convenient below in comparing certain lines which are alike in J'.[96] To make

---

[93] This is possible, since for the $^2\Pi$ levels there is a one to one correspondence between the rotational levels of cases a and b (cf. Part II*b*, pp. 112–13). Regular $^2\Pi_{\frac{1}{2}}$ levels of case a correspond to T_1 levels of case b, regular $^2\Pi_{1\frac{1}{2}}$ levels to T_2 levels.

[94] Except for this, another notation (cf. section *J2d*) would be more convenient as well as more appropriate.

[95] Cf. caption of Fig. 28 in regard to the significance of O and S in the symbols $^OP_{12}$ and $^SR_{21}$.

[96] Eqs. (76) can be transformed into the usual explicit functions of J'' (conventionally written simply as J) by substituting the expressions $J-1$, J, $J+1$ for the symbol J' in the equations of P, Q, and R branches respectively.

clear what is being done, the steps are given in detail for ${}^OP_{12}$ as an example (Eqs. 76*a*).

$$\begin{aligned}
{}^OP_{12}(J') &= T_{1c}'(J') - T_2''(J'+1) = \nu_1 + \tfrac{1}{2}a(J'+\tfrac{1}{2}) + B_1J'(J'+1) \\
&\quad + \tfrac{1}{2}\gamma(J'+2\tfrac{1}{2}) - B(J'+1\tfrac{1}{2})(J'+2\tfrac{1}{2}) + \cdots \\
&= \nu_1 + \tfrac{1}{4}(a+5\gamma-15B) - (4B - B_1 - \tfrac{1}{2}a - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_1 - B)J'^2 + \cdots \qquad (76a)
\end{aligned}$$

$$\begin{aligned}
P_1(J') &= T_{1d}'(J') - T_1''(J'+1) = \nu_1 - \tfrac{1}{4}(a+\gamma+3B) \\
&\quad - (2B - B_1 + \tfrac{1}{2}a + \tfrac{1}{2}\gamma)J' + (B_1 - B)J'^2 + \cdots \qquad (76b)
\end{aligned}$$

$$\begin{aligned}
{}^PQ_{12}(J') &= T_{1d}'(J') - T_2''(J') = \nu_1 - \tfrac{1}{4}(a - 3\gamma + 3B) \\
&\quad - (2B - B_1 + \tfrac{1}{2}a - \tfrac{1}{2}\gamma)J' + (B_1 - B)J'^2 + \cdots \qquad (76c)
\end{aligned}$$

$$\begin{aligned}
Q_1(J') &= T_{1c}'(J') - T_1''(J') = \nu_1 + \tfrac{1}{4}(a+\gamma+B) + (B_1 + \tfrac{1}{2}a - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_1 - B)J'^2 + \cdots \qquad (76d)
\end{aligned}$$

$$\begin{aligned}
{}^QR_{12}(J') &= T_{1c}'(J') - T_2''(J'-1) = \nu_1 + \tfrac{1}{4}(a+\gamma+B) + (B_1 + \tfrac{1}{2}a + \tfrac{1}{2}\gamma)J' \\
&\quad + (B_1 - B)J'^2 + \cdots \qquad (76e)
\end{aligned}$$

$$\begin{aligned}
R_1(J') &= T_{1d}'(J') - T_1''(J'-1) = \nu_1 - \tfrac{1}{4}(a - 3\gamma + 3B) \\
&\quad + (2B + B_1 - \tfrac{1}{2}a - \tfrac{1}{2}\gamma)J' + (B_1 - B)J'^2 + \cdots \qquad (76f)
\end{aligned}$$

$$\begin{aligned}
P_2(J') &= T_{2d}'(J') - T_2''(J'+1) = \nu_2 + \tfrac{1}{4}(5\gamma - 15B) - (4B - B_2 - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76g)
\end{aligned}$$

$$\begin{aligned}
{}^QP_{21}(J') &= T_{2c}'(J') - T_1''(J'+1) = \nu_2 - \tfrac{1}{4}(\gamma + 3B) - (2B - B_2 + \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76h)
\end{aligned}$$

$$\begin{aligned}
Q_2(J') &= T_{2c}'(J') - T_2''(J') = \nu_2 - \tfrac{1}{4}(-3\gamma + 3B) - (2B - B_2 - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76i)
\end{aligned}$$

$$\begin{aligned}
{}^RQ_{21}(J') &= T_{2d}'(J') - T_1''(J') = \nu_2 + \tfrac{1}{4}(\gamma + B) + (B_2 - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76j)
\end{aligned}$$

$$\begin{aligned}
R_2(J') &= T_{2d}'(J') - T_2''(J'-1) = \nu_2 + \tfrac{1}{4}(\gamma + B) + (B_2 + \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76k)
\end{aligned}$$

$$\begin{aligned}
{}^SR_{21}(J') &= T_{2c}'(J') - T_1''(J'-1) = \nu_2 - \tfrac{1}{4}(-3\gamma + 3B) + (2B + B_2 - \tfrac{1}{2}\gamma)J' \\
&\quad + (B_2 - B)J'^2 + \cdots \qquad (76l)
\end{aligned}$$

In Eqs. (76), $\nu_1 = W_1 - W$, $\nu_2 = W_2 - W$, and, it should be noted, $\nu_2 > \nu_1$ always (approximately, $\nu_2 - \nu_1 = |A|$). It should also be noted that the B's are always larger (usually much larger) than a and γ. Fig. 29 shows graphically by means of Fortrat diagrams (cf. Fig. 19), for the ${}^2\Pi, {}^2\Sigma^+$ bands of HgH, the forms of the various branches given by Eqs. (76).

The equations for a ${}^2\Pi$(case a),${}^2\Sigma^-$ transition are exactly the same as Eqs. (76), except that the subscripts c and d in the definitions of the branches must be interchanged, and corresponding to this (cf. Eqs. 75*a*,*b*), every a in the equations must be replaced by $-a$.

2a. *Coalescence of branches: eight-branch bands when* $\gamma = 0$. Some relationships between the different branches given by Figs. 28–29 and Eqs. (76) have considerable interest for an understanding of certain special cases, and of the empirical structure in the general case. These relationships, which can be obtained very simply by subtraction using suitable pairs of equations in the Eqs. (76) group, are as follows:

$$^{P}Q_{12}(J') - P_1(J') = \gamma(J' + 1) = \gamma(K'' + \tfrac{1}{2}) \tag{77a}$$

$$^{Q}R_{12}(J') - Q_1(J') = \gamma J' = \gamma(K'' + \tfrac{1}{2}) \tag{77b}$$

$$Q_2(J') - {}^{Q}P_{21}(J') = \gamma(J' + 1) = \gamma(K'' + \tfrac{1}{2}) \tag{77c}$$

$$R_2(J') - {}^{R}Q_{21}(J') = \gamma J' = \gamma(K'' + \tfrac{1}{2}). \tag{77d}$$

From these equations (cf. also Figs. 28 and 29), it can be seen that the eight branches involved in Eqs. (77) form four pairs such that the members of each pair, e.g., $^{P}Q_{12}(J')$ and $P_1(J')$, differ in wave-number by the interval $\gamma(K''+\frac{1}{2})$. This interval is the doublet separation of two levels $J'' = K'' \pm \frac{1}{2}$ of the $^2\Sigma$ state.[97] Thus the magnitude (and sign) of the $^2\Sigma$ doublet separations can be read directly from the spectrum. Equations for the $^2\Pi$ doublet separations in terms of differences between the frequencies of two band-lines can also be given (cf. Eqs. 85*a*, 85*b*).

We note further that branches such as $^{P}Q_{12}$ and P_1 which form a pair of the kind just discussed, are usually relatively near together on the Fortrat diagram (Fig. 29). In fact, such pairs of branches become fused into apparent single branches if the $^2\Sigma$ doublet separations become vanishingly small ($\gamma \sim 0$).[97] This often occurs, and the number of branches is then apparently reduced from twelve to eight (four single and four double branches). The necessary condition $\gamma \sim 0$ is, however, usually fulfilled only if A is not very large, since γ is usually approximately proportional to A. Hence these eight-branch bands are usually to be expected only for rather small values of A, where there are at the same time other deviations from the limiting case of $^2\Pi$ (case *a*) $\rightarrow {}^2\Sigma$ (cf. section *J*3, p. 141 for further discussion and examples).

2b. *Forms of branches; position of heads.* The forms of the branches (i.e. the ν's as functions of J') can be better understood if we first rewrite Eqs. (76) neglecting a and γ. If further we make the substitution $J' = -(m+1)$ in the P branches and the related $^{P}Q_{12}$ and Q_2 branches, and the substitution $J' = m$ in the R, Q_1, and $^{R}Q_{21}$ branches, Eqs. (76) take the following forms:

$$^{O}P_{12}(m) \text{ and } R_1(m): \nu = \nu_1 - \tfrac{3}{4}B'' + (B' + 2B'')m + (B' - B'')m^2 \tag{78a}$$

$$P_1(m) = {}^{P}Q_{12}(m), \text{ and } Q_1(m) = {}^{Q}R_{12}(m): \nu = \nu_1 + \tfrac{1}{4}B'' + B'm + (B' - B'')m^2 \tag{78b}$$

$$P_2(m) \text{ and } {}^{S}R_{21}(m): \nu = \nu_2 - \tfrac{3}{4}B'' + (B' + 2B'')m + (B' - B'')m^2 \tag{78c}$$

$$^{Q}P_{21}(m) = Q_2(m), \text{ and } {}^{R}Q_{21}(m) = R_2(m): \nu = \nu_2 + \tfrac{1}{4}B'' + B'm + (B' - B'')m^2 \tag{78d}$$

---

[97] From Fig. 28 one sees directly that, independent of the exact forms assumed for the terms in Eqs. (75), intervals such as $^{P}Q_{12}(J') - P_1(J')$ represent exactly the doublet separations of the $^2\Sigma$ levels, and vanish if the latter vanish.

In these equations, B_1 and B_2 have been written B', B has been written B''. In these equations m assumes negative half-integral values in the P, $^PQ_{12}$, and Q_2 branches, positive half-integral values in the R, Q_1, and $^RQ_{21}$ branches. It is instructive to compare these equations with those for P, Q, and R branches in ordinary case $a \rightarrow$ case a transitions. Here (cf. Eqs. 15, 58 and 59) we have essentially

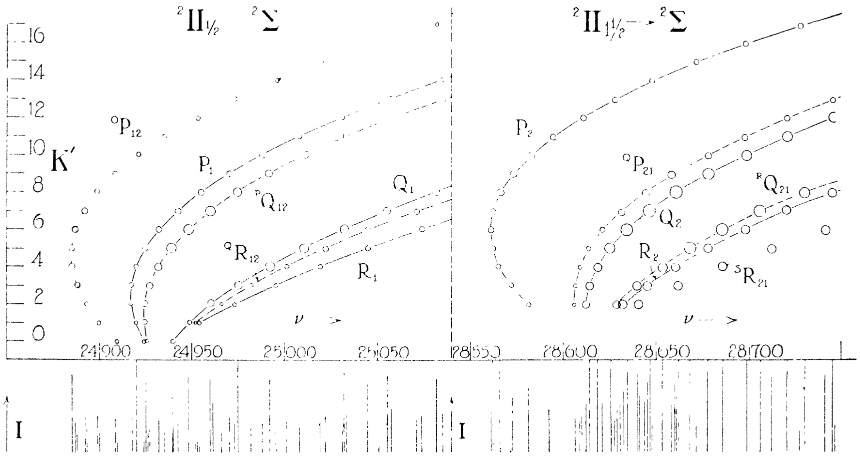


Fig. 29. Fortrat diagram (cf. Fig. 19) for HgH, corresponding to Fig. 28, and plotted as a function of the parameter K' (cf. caption of Fig. 28). K' is the same as $|M|$ of Fig. 30 (cf. caption of Fig. 30) and other figures except in the following cases: $^OP_{12}$, $|M| = K'+2$; P_1, $^PQ_{12}$, and P_2, $|M| = K'+1$; $^SR_{21}$, $|M| = K'-1$. In comparing Fig. 29 with Fig. 30 and other figures, the K' scale in Fig. 29 can be taken as an $|M|$ scale if the branches just mentioned are shifted (usually up) by $|M| - K'$ units.

The intensities I (cf. Eq. 53c) of the lines have been calculated for a rotational energy distribution in each of the initial states $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ corresponding to thermal equilibrium at $T = 900°K$, but assuming g of Eq. (53c) the same for $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$. These calculated intensities are proportional to the *areas* of the small white circles. The calculated values make use of the i factors (cf. Eq. 53c) calculated by Kapuściński and Eymers,[98] and agree rather well with the measurements made by them, except that the observed g factors are not quite equal for $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$.

The actual appearance of the band is indicated in the lower part of the diagram. The heights of the lines are shown proportional to their I values. When two lines fall very close together on the ν scale, they have been represented by a single line with an I value equal to the sum of those of its components.

If in Eqs. (75d), (75e) and (76), we had had $\gamma = 0$, the pair of branches P_1 and $^PQ_{12}$ would become in effect a single branch occupying very nearly a median position. An analogous statement applies to other pairs Q_1 and $^QR_{12}$, $^QP_{12}$ and Q_2, and $^RQ_{21}$ and R_2. Each of these pairs, it should be noted, consists of what in case b would be a main and a satellite branch. The positions of the unpaired branches $^OP_{12}$, R_1, P_2, and $^SR_{21}$ would also shift considerably if we had $\gamma = 0$. If we had $a = 0$ in the $^2\Pi_{\frac{1}{2}}, {}^2\Sigma$ band, the branches $^OP_{12}$, Q_1 and $^QR_{12}$ would be shifted toward the left as compared with their present positions, the branches P_1, $^PQ_{12}$, and R_1 toward the right. This would make the $^2\Pi_{\frac{1}{2}}, {}^2\Sigma$ band nearly a replica, except for missing lines, of the $^2\Pi_{1\frac{1}{2}}, {}^2\Sigma$ band.

In Figs. 28 and 29, we have $B' > B''$, and heads are formed on the P_2, $^QP_{12}$, Q_2, and on the $^OP_{12}$, P_1 and $^PQ_{12}$ branches. If we had had $B' < B''$, the heads would occur on the other six branches. For $a = 0$ and $\gamma = 0$ the positions of the various heads would be given by Eqs. (79).

$$P(M) \text{ and } R(M)\colon \nu = \nu_0 + (B' + B'')M + (B' - B'')M^2 \qquad (58')$$

$$Q(M)\colon \nu = \nu_0 + (B' - B'')M(M + 1). \qquad (59')$$

In the P branch, M has negative integral values, in the Q and R branches, it has positive integral values. If the forms of the P, Q, and R branches in Eqs. (58′) and (59′) are taken as standard for P, Q, and R, the P and R branches (and their associated Q branches) in Eqs. (78*a*) and (78*c*) may be described as $\frac{3}{2}P$- and $\frac{3}{2}$-R form, those in Eqs. (78*b*) and (78*d*) as $\frac{1}{2}P$- and $\frac{1}{2}R$-form.

If the M or m value of the band-head is denoted by M_{head} or m_{head}, and the displacement of the band-head from the position for which $M=0$ or $m=0$ is denoted by $\Delta\nu_{head}$, we have the following expressions (cf. Part II*a*, Eq. 16) for the heads of the branches which are given by Eqs. (58′), (59′), and (78):

P or R of (58′): $M_{head} \sim -(B' - B'')/2C$, and

$$\Delta\nu_{head} \sim -(B' + B'')^2/4C \qquad (16')$$

Q of (59′): $M_{head} = 0$, $\Delta\nu_{head} = 0$ (16″)

${}^{O}P_{12}$ or R_1 of (78*a*), and P_2 or ${}^{S}R_{21}$ of (78*c*):

$$m_{head} \sim -(B' + 2B'')/2C, \text{ and } \Delta\nu_{head} \sim -(B' + 2B'')/4C \qquad (79a)$$

$P_1 = {}^{P}Q_{12}$ or $Q_1 = {}^{Q}R_{12}$, and ${}^{Q}P_{21} = Q_2$ or ${}^{R}Q_{21} = R_2$:

$$m_{head} \sim -B'/2C, \text{ and } \Delta\nu_{head} \sim -B'^2/4C. \qquad (79b)$$

In these equations, C stands for $B'-B''$. In Eqs. (16′), (79*a*), and (79*b*), of course only half the branches named can have heads. E.g. in Eq. (16′), *either* the P or the R branch has a head according as M_{head} comes out negative or positive. Similar statements apply to the other equations. If $B'>B''(C>0)$, the P-form branches have heads, if $B'<B''$, the R-form branches have heads (cf. also Figs. 25 and 26).

Starting with the simplified equations (78) and (79), the reader can perhaps best see for himself, with the help of Eqs. (76) and Figs. 28 and 29, how the forms of the branches and the positions of the heads change when we have $a\neq 0$ and $\gamma\neq 0$. It should not be forgotten that a and γ sometimes have negative values.

2c. *Intensity relations.* For the ideal limiting case of a ${}^2\Pi$ state with $A=+\infty$, the work of Hill and Van Vleck[89] shows that the intensity factors i of Eqs. (53) should be given in any ${}^2\Pi(\text{case } a)\rightarrow{}^2\Sigma(\text{case } b)$ band by the following equations (cf. section 2*d* in regard to the case $A=-\infty$):

$${}^{O}P_{12} \text{ and } P_1\colon i = (2J' + 1)(2J' + 3)/32(J' + 1) \qquad (80a)$$

$${}^{P}Q_{12} \text{ and } Q_1\colon i = (2J' + 1)^3/32J'(J' + 1) \qquad (80b)$$

$${}^{Q}R_{12} \text{ and } R_1\colon i = (4J'^2 - 1)/32J' \qquad (80c)$$

$$P_2 \text{ and } {}^{Q}P_{21}\colon i = (4J'^2 - 1)/32(J' + 1) \qquad (80d)$$

$$Q_2 \text{ and } {}^{R}Q_{21}\colon i = (4J'^2 - 1)(2J' + 3)/32J'(J' + 1) \qquad (80e)$$

$$R_2 \text{ and } {}^{S}R_{21}\colon i = (2J' + 1)(2J' + 3)/32J'. \qquad (80f)$$

Eqs. (80*a*)–(80*c*) apply to ${}^2\Pi_{\frac12},{}^2\Sigma$ and Eqs. (80*d*)–(80*f*) to ${}^2\Pi_{1\frac12},{}^2\Sigma$.

In practise the nearest approach to the intensity relations predicted by Eqs. (80) is found in the HgH bands, where $A/B = +560$. Even with such a large value of A/B, there are rather pronounced departures from the relations of Eqs. (80) toward those of case *b*. Kapuŝcínski and Eymers have found[98] in careful measurements that the observed relative intensities in the HgH bands are in agreement with those calculated from the general equations of Hill and Van Vleck for $A/B = +560$. These intensity relations are shown in Fig. 29. The observed variation of intensity with J' corresponds fairly closely, for the lower values of J', to a thermal distribution of rotational energy with a temperature of about 900°*K*, but deviates considerably from this at higher J' values. After making allowance for the ν^4 factor, the g values (cf. Eq. 53*c*) are apparently about 25% larger for the $^2\Pi_{\frac{1}{2}}, {}^2\Sigma$ than for corresponding $^2\Pi_{1\frac{1}{2}}, {}^2\Sigma$ bands. This difference is, however, negligible compared with the ratio of the g values (about 360:1 in favor of $^2\Pi_{\frac{1}{2}}, {}^2\Sigma$) calculated for thermal equilibrium at 900°*K*. Evidently the factors determining the distribution between $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ are quite different from those determining the rotational distributions (cf. discussion preceding Eq. 53*c*).

2d. $^2\Pi$(*case a*),$^2\Sigma$ *transitions with inverted* $^2\Pi$. Although Eqs. (75)–(79) all hold for inverted as well as for regular $^2\Pi$ states in $^2\Pi, {}^2\Sigma$ transitions, the branches begin with different J' values when $A < 0$ in the $^2\Pi$ state than when $A > 0$. This is because for $A < 0$, unlike $A > 0$, the $^2\Pi_{1\frac{1}{2}}$ levels are classified as T_1 (cf. Part II*b*, pp. 112–13) and begin with $J = 1\frac{1}{2}$ while the $^2\Pi_{\frac{1}{2}}$ levels are classified as T_2 and begin with $J = \frac{1}{2}$. Physically, this difference in respect to the first lines of the branches is more apparent than real, since it results solely from our use of case *b* notation for the $^2\Pi$ level. If we had *defined* all $^2\Pi_{\frac{1}{2}}$ levels as T_1 and all $^2\Pi_{1\frac{1}{2}}$ levels as T_2 for inverted as well as for regular $^2\Pi$, then the two cases $A > 0$ and $A < 0$ would be identical in respect to the J' value of the first line in each branch as well as in respect to the validity of Eqs (75)–(79). The intensity equations (80) would also probably[99] apply unchanged if we defined all $^2\Pi_{\frac{1}{2}}$ levels as T_1 and all $^2\Pi_{1\frac{1}{2}}$ levels as T_2, although they surely do not apply with the notation used here. With the revised definitions, we should have $\nu_1 > \nu_2$ when $A > 0$ and $\nu_2 < \nu_1$ when $A > 0$, instead of $\nu_2 > \nu_1$ for both cases as is true with the present definitions.

2e. $^2\Sigma, {}^2\Pi$(*case a*) *transitions*. As can easily be shown by comparison of Fig. 28 with a corresponding diagram for a $^2\Sigma, {}^2\Pi$ transition, the equations (76)–(77) given above for $^2\Pi$(case *a*),$^2\Sigma$ transitions can readily be transformed into the corresponding equations for $^2\Sigma, {}^2\Pi$ transitions in the following way: (1) make the following substitutions of symbols: P for R and R for P, subscript 12 for 21 and vice versa, T' for T'' and vice versa, J'' for J', K' for K''. All other quantities stand as before, but ν_1 and ν_2 are now defined by $\nu_1 = W - W_1$, $\nu_2 = W - W_2$. (2) In Eqs. (76), reverse the sign of all quantities

---

[98] W. Kapuŝciński and J. G. Eymers, Zeits. f. Physik **54**, 246 (1929); J. G. Eymers, Zeits. f. Physik **63**, 396 (1930). In these papers the quantities here designated as i are called $f(j)$.

[99] Intensity equations are not given for $A < 0$ by Hill and Van Vleck, but it is fairly obvious that the equations would be the same as for $A > 0$ *if we define* T_1 and T_2 as corresponding to $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$.

on the right-hand side after the symbol ν_1 or ν_2. In Eqs. (77), reverse the *order* of the two symbols on the *left-hand* side.

To illustrate the meaning of these rules, two examples will be given. By transforming Eq. (76*a*) for ${}^{O}P_{12}(J')$ in the manner indicated, we get:

$$\begin{aligned} {}^{S}R_{21}(J) &= T_2'(J''+1) - T_{1c}''(J'') \\ &= \nu_1 - \tfrac{1}{4}(a + 5\gamma - 15B) + (4B - B_1 - \tfrac{1}{2}a - \tfrac{1}{2}\gamma)J + (B - B_1)J^2 \quad (81a) \end{aligned}$$

Eqs. (81*b*)–(81*f*) can be obtained in a similar way. The J' and J'' values of the first lines in each branch in Eqs. (81) can most conveniently be read from a diagram similar to Fig. 28 (not given here).

From Eq. (77*a*) for ${}^{P}Q_{12}(J') - P_1(J')$ we get

$$R_1(J) - {}^{R}Q_{21}(J) = \gamma(J''+1) = \gamma(K' + \tfrac{1}{2}). \qquad (82a)$$

When $\gamma \rightarrow 0$, we have apparent eight-branch bands as in the ${}^2\Pi, {}^2\Sigma$ case.

Equations similar to (78) and (79) can be obtained for ${}^2\Sigma, {}^2\Pi$ transitions after substituting $J'' = m$ in the case of the R and related Q branches, $J'' = -(m+1)$ in that of the P and related Q branches, and putting $B = B'$, B_1 and $B_2 = B''$, in Eqs. (81). [The desired equations cannot be obtained directly by substitution in Eqs. (78)–(79) themselves.] For example, we get in this way

$$P_1(m) \text{ and } {}^{S}R_{21}(m)\colon \nu = \nu_1 + (15/4)B' + (4B' - B'')m + (B' - B'')m^2 \qquad (83a)$$

From this,

$$m_{head} \sim -(4B' - B'')/2C, \text{ and } \Delta\nu_{head} \sim -(4B' - B'')^2/4C. \qquad (84a)$$

The forms of the branches are evidently similar to those of ${}^2\Pi, {}^2\Sigma$ bands.

The intensity relations are probably given[100] by a set of equations obtainable from Eqs. (80) by interchanging the symbols P and R, and the subscripts 12 and 21, and substituting J'' for J'.

3. ${}^2\Pi, {}^2\Sigma$ *and* ${}^2\Sigma, {}^2\Pi$ *bands with* ${}^2\Pi$ *intermediate between cases a and b.* We wish now to see how the structure and intensity relations of ${}^2\Pi, {}^2\Sigma$ bands vary with the value of A/B in the range of intermediate cases[90] from case *a* regular ${}^2\Pi(A >> B)$ through case *b* ${}^2\Pi(|A|/B \text{ small})$ to case *a* inverted ${}^2\Pi(-A >> B)$. We can do this best in connection with a series of Fortrat diagrams (Figs. 29 and 30). These diagrams have been drawn from the equations of the various branches, defined in terms of the T''s and T''s as in the *first equality* given in each of the Eqs. (76): for example, $P_1(J) = T_{1d}'(J-1) - T_1''(J)$ if the ${}^2\Sigma$ state is ${}^2\Sigma^+$ (cf. last paragraph of section $J2$ in regard to ${}^2\Pi, {}^2\Sigma^-$ bands). [We are now using the conventional definitions in terms of J'' (identical with J as here used) instead of in terms of J' as in Eqs. (76).[96]] The T''s are given in general by the equation of Hill and Van Vleck (Eq. 37) instead of by the special equations (75*a*)–(75*c*) which hold for large $|A|/B$ values and which we have used in getting the second equalities in Eqs. (76). There is not much point in giving for the general case explicit equations like Eqs. (76) in terms

---

[100] The intensity equations are not given explicitly for this case by Hill and Van Vleck, but the necessary alterations in their equations for ${}^2\Pi(\text{case } a), {}^2\Sigma$ transitions are fairly obvious.

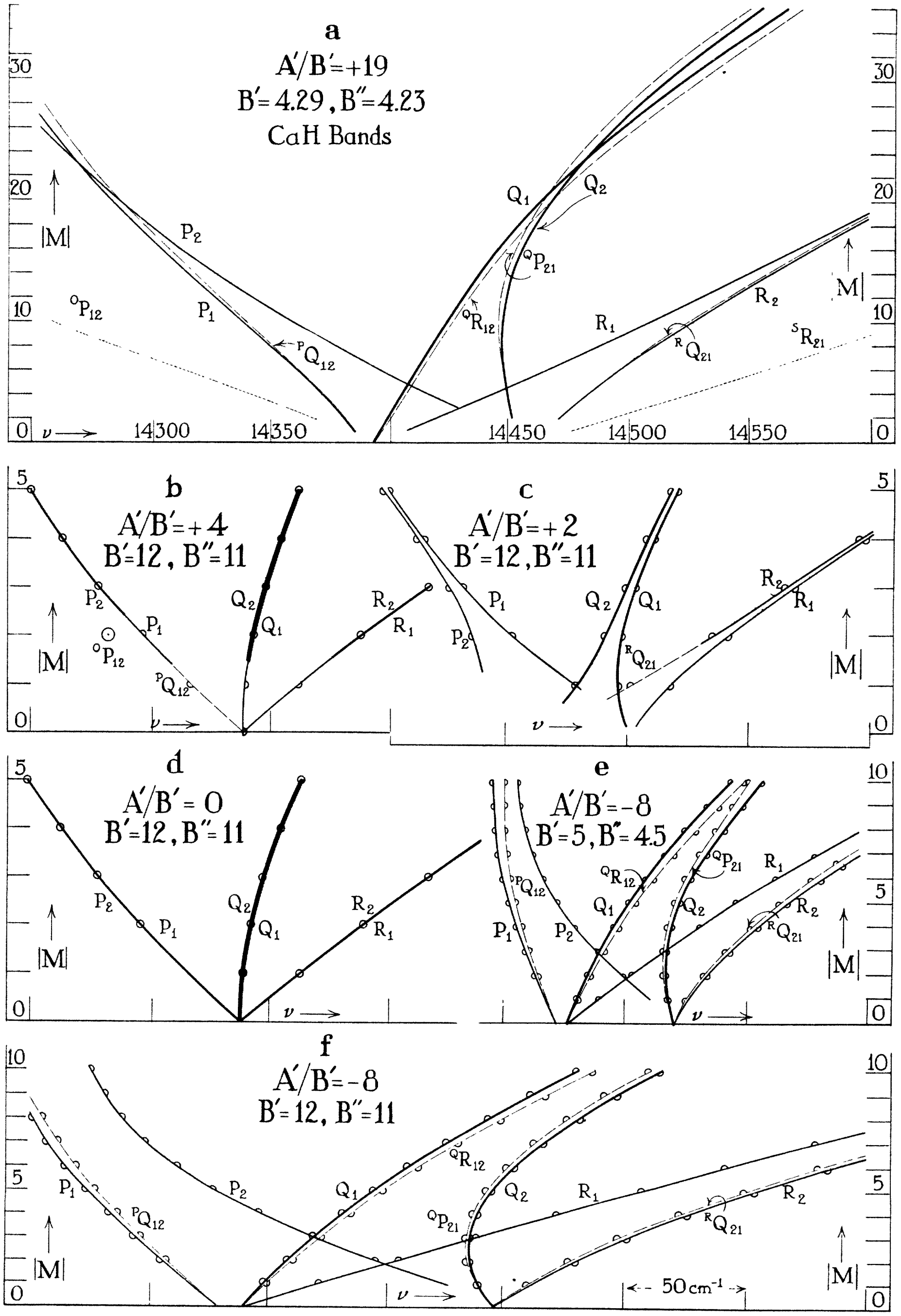

a
A′/B′=+19
B′=4.29, B″=4.23
CaH Bands
|M|
P₂
P₁
ᴼP₁₂
ᴾQ₁₂
Q₁
Q₂
ᑫP₂₁
ᑫR₁₂
R₁
R₂
ᴿQ₂₁
ˢR₂₁
ν
14300
14350
14450
14500
14550
0
10
20
30
b
A′/B′=+4
B′=12, B″=11
P₂
P₁
ᴼP₁₂
ᴾQ₁₂
Q₂
Q₁
R₂
R₁
c
A′/B′=+2
B′=12, B″=11
P₁
P₂
Q₂
Q₁
ᴿQ₂₁
R₂
R₁
5
d
A′/B′=0
B′=12, B″=11
P₂
P₁
Q₂
Q₁
R₂
R₁
e
A′/B′=−8
B′=5, B″=4.5
ᴾQ₁₂
P₁
P₂
ᑫR₁₂
Q₁
ᑫP₂₁
Q₂
R₁
R₂
ᴿQ₂₁
f
A′/B′=−8
B′=12, B″=11
P₁
ᴾQ₁₂
P₂
Q₁
ᑫR₁₂
ᑫP₂₁
Q₂
R₁
R₂
ᴿQ₂₁
50 cm⁻¹

FIG. 30

Fig. 30. Structure of ${}^2\Pi,{}^2\Sigma$ bands for a variety of A/B values in the ${}^2\Pi$ state. For the significance of the *full*, *dashed*, and *dotted lines*, cf. the caption of Fig. 28. The relative *intensities* of the branches are roughly indicated by the heaviness of the curves. [The variation of intensity with M in each branch is not indicated, but can be judged approximately by comparison with Figs. 19 and 29.] For energy level diagrams corresponding to some of the cases shown, cf. Fig. 15 and Ref. 90. The Fortrat diagrams are plotted against $|M|$ values, where M is defined as follows in accordance with the K values of case b: $M=-K''$ for $K'-K''=-2$ or -1, $M=K''$ for $\Delta K=0$, $M=+K''+1$ for $K'-K''=+1$ or $+2$. The *ν scale is the same in all the diagrams.*

Fig. 30a, which is based on data[90] for CaH, using the J assignments given by Watson and Bender for the Q branches, shows how the two widely separated main branches of each kind (P_1 and P_2, Q_1 and Q_2,R_1 and R_2), corresponding to the two states ${}^2\Pi_{\frac{1}{2}}$ and ${}^2\Pi_{1\frac{1}{2}}$ of case a, rapidly approach each other with increasing J, in the transition to case b. In the contraction of these doublets, e.g. $P_1(K)-P_2(K)$, with increasing J, various cases are in general possible, depending on the values of γ' and γ'' (cf. Eq. 85). Under some circumstances, the branches P_1 and P_2 eventually cross, likewise Q_1 and Q_2, and R_1 and R_2. This case occurs in CaH, and is shown in Fig. 30a. In Fig. 30a the separations of the satellite branches from the corresponding main branches have been *exaggerated eightfold* to make them easily visible. The positions of the satellite lines, although not given in Ref. 90, have been calculated from the data given there.

For smaller values of A in the ${}^2\Pi$ state than in Fig. 30a, doublet separations such as P_1-P_2 approach zero more rapidly with increasing $|M|$ (cf. Figs. 30c, e, f). For $A/B\backsim 0$, branches such as P_1 and P_2 practically coincide for all J values, except insofar as they are kept apart by spin doubling ($\gamma\neq 0$) in the ${}^2\Sigma$ state (cf. Fig. 25 and Eq. 85), or by the existence of a $\gamma\neq 0$ in the ${}^2\Pi$ state (cf. Eq. 85). For $A/B=+4$, the relations are exactly the same as for $A/B=0$, except for the lines of very low M values. In labelling these lines, the anomalous level with $J=\frac{1}{2}$ is treated as a T_1 level, with $K=0$ (cf. caption of Fig. 28). For $A/B=2$, however, it is treated as a T_2 level with $K=1$. In comparing Figs. 30b and c, it should be noted that ${}^OP_{12}[2]$, ${}^PQ_{12}[1]$, and $Q_1[0]$ in 30b are the analogues of $P_2[2]$, $Q_2[1]$, and ${}^RQ_{21}[1]$ in 30a (the numbers in brackets are $|M|$ values). The different nomenclature in 30a and b is a result of the different classification of the level with $J=\frac{1}{2}$ .In Fig. 30b, c, d, $\gamma'=\gamma''=0$ is assumed, since $\gamma'\backsim 0$, $\gamma''\backsim 0$ are usually expected when A/B is small. In Figs. 30b to 30f the forms of the branches are made more obvious by continuing the curves to $|M|=0$ or 1. The actual band-lines are indicated by circles or semi-circles.

The satellite branches (dashed lines) get weaker and weaker, except for the very smallest J values, with decreasing $|A|$ of the ${}^2\Pi$ state. They usually at the same time, because of $\gamma\rightarrow 0$ for the ${}^2\Sigma$ state, get closer and closer to the corresponding main branches, and usually cannot be separated from the latter when $|A|$ is small in the ${}^2\Pi$ state. In Fig. 30 b, c, d, since we have assumed $\gamma''=0$, the satellite lines coincide, except for the first line in a branch in one or two cases, with the corresponding main branch lines. Moreover, their intensities here are negligible except for the very lowest K values. In Fig. 30a, e,f, the satellite branches are slightly separated from their main branches (the separations shown are *greatly exaggerated* for the sake of clearness) but still have low intensity, while in Fig. 29 the satellite branches are strong and quite distinct from the main branches.

The lines with $\Delta K=\pm 2$ (dotted lines) approach zero intensity as $|A|\rightarrow 0$. This is indicated in the figure by their omission for small A values except in the special case of the line ${}^OP_{12}(1\frac{1}{2})$ when $A/B=+4$. They are *also omitted* in Fig. 30e, f, for the sake of simplicity, although they should be present in low intensity.

The *two* diagrams Figs. 30e and f have been included in order to call attention to the effect on the band structure, with given A/B, of the magnitude of A or B. Allowance should be made for this effect in comparing diagrams in Fig. 30 which have different B values, also in comparisons with Fig. 29. It should also be noted that some of the differences between the various diagrams in Figs. 29 and 30 are the result of differences in the quantity $(B'+B'')/(B'-B'')$ which governs the formation of heads (cf. Eq. 16 of Part I and Eqs. 79).

of J values, and we shall not do so. All that is important can be seen from the term-forms T' and T'', energy-level diagrams (cf. Fig. 15, Ref. 90, and Fig. 28), and Fortrat diagrams (Figs. 29, 30).

In illustration of the discussion of $^2\Pi,^2\Sigma$ bands we shall include a few examples of $^2\Sigma,^2\Pi$ bands, which show essentially similar behavior (cf. Eqs. 81–84 and related text).

Before discussing the changes which occur as $|A|/B$ is varied, it should be mentioned that for all intermediate values of $|A|/B$ of the $^2\Pi$ state, just as in the limiting cases $|A|=\infty$ (cf. Eqs. 80) and $A\sim 0$ (case b, Eqs. 73 and Fig. 25), the intensity relation $Q_i>R_i>P_i$ is predicted[89] and found in $^2\Pi,^2\Sigma$ transitions, among the branches with single as well as among those with double subscripts. In $^2\Sigma,^2\Pi$ transitions, $Q_i>P_i>R_i$ is expected and found.

Turning now to the effects of varying A/B, let us consider the series of cases, (1) $A/B=+560$ (HgH, good case a, Fig. 29) and $A/B=-250$ (good case a inverted $^2\Pi$, *not shown*), (2) $A/B=+19$ and -8 (typical intermediate cases, Figs. 30*a,e,f*), and (3) $A/B=4$, 2, 0 (all essentially case b, Figs. 30*b,c,d*). The changes which occur as $|A|/B\rightarrow 0$ are similar, but not quite the same, in the two series with positive and with negative A values. Case b is more rapidly approached for the positive A values, since for the critical value $A/B=+4$, case b relations exist, in most respects, just as for $A=0$, while for negative A's there is no similar critical value of A/B.

The transition toward case b shows itself first, while $|A|$ is still fairly large, at high J values (cf. Part II*b*, top of p. 106). Certain rotational levels of the $^2\Pi_{\frac{1}{2}}$ state tend to form pairs $(J=K\pm\frac{1}{2})$ with levels of the $^2\Pi_{1\frac{1}{2}}$ state (cf. Fig. 15). Corresponding to this, certain branches in the spectrum (the main branches, full lines in Figs. 29, 30), tend to become paired: R_2 with R_1, Q_2 with Q_1, and P_2 with P_1. Meantime the satellite branches Q_{21}, P_{21}, R_{12}, and Q_{12} (dashed lines in Figs. 29, 30) become much weaker relative to corresponding main branches (R_2, Q_2, Q_1, P_1 respectively, in $^2\Pi,^2\Sigma$ bands). At the same time, the branches $^SR_{21}$ and $^OP_{12}$ (for $^2\Sigma,^2\Pi$ as well as for $^2\Pi,^2\Sigma$), which do not become fused with other branches, show an even more rapid decrease in intensity compared with the main branches. These branches are shown by dotted lines in Figs. 28 and 29. [In considering intensity relations in intermediate cases, it should be remembered that even for large A/B values such as that of the $^2\Pi$ of HgH (cf. section *J2c*) there is a considerable departure, except for low J values, from the intensity relations (Eqs. 80) which would hold for $A/B=+\infty$, toward those of case b.]

If $|A|$ is made smaller and smaller, the effects mentioned become more and more pronounced, and become important even at low J values.

[The reasons why the branches with double subscripts fade out as $A\rightarrow 0$ or $J\rightarrow\infty$ in the $^2\Pi$ state can easily be understood qualitatively. In case b, where the quantum number K is sharply defined, we have the two selection rules $\Delta K=0,\ \pm 1$ and $\Delta J=0,\ \pm 1$. Branches with $\Delta K=\pm 2$ are strictly ruled out. The branches $^SR_{21}$ and $^OP_{12}$ of $^2\Pi$(case a),$^2\Sigma$ go over into branches with $\Delta K=+2$ and -2 in $^2\Pi$(case b),$^2\Sigma$. Hence these branches fade out more and more as K becomes more sharply defined for the $^2\Pi$ levels, and disappear in case *b*. The main and satellite branches, however, all fulfill the case *b* selection rules and so do not disappear. In the main branches $\Delta J = \Delta K$, which gives strong lines in case *b*, but in the satellite branches $\Delta J \neq \Delta K$, and this causes the latter to have, except for very small K values, very low intensities in case *b* (cf. Eqs. 72–74 and related text).]

Since the $^2\Sigma$ doublet separations usually decrease with $|A|$, the satellite branches, in addition to becoming weaker as $|A|$ decreases, come closer to the corresponding main branches (cf. Eqs. 77, which hold for all values of A/B, and accompanying discussion), or often become practically fused with them, usually long before R_1 and R_2, Q_1 and Q_2, R_1 and R_2 in turn become fused. Fig. 29 shows the main and satellite branches well separated, while Fig. 30*a*, *e* show them almost fused. If the main and satellite branches become fused, we have bands of the eight-branch type. It should be noted that in eight-branch bands, the two outer branches $^SR_{21}$ and $^OP_{12}$ are usually decidedly weaker than the other branches, since the eight-branch type does not occur unless $|A|$ is fairly small. Whether or not the main and satellite branches become fused,—usually they do,—as $A \rightarrow 0$, the satellite and the $^SR_{21}$ and $^OP_{12}$ branches fade to practically zero intensity, giving an essentially six-branch type as in case *b* (cf. Fig. 30*b*, *c*, *d*).

Examples[90] of typical eight-branch bands are the NO γ bands ($^2\Sigma$,$^2\Pi$), with $A/B = +29$ in the $^2\Pi$ state, and the red CN, the CO$^+$, and BO α bands (all $^2\Pi$,$^2\Sigma$ with $A/B = -34$, -79, and -90). Other bands which strictly speaking are twelve-branch bands like the HgH, CdH, and ZnH bands, but in which the outer branches $^OP_{12}$ and $^SR_{21}$ and the satellite branches are much weaker than the main branches so that the bands are practically six-branch bands nearly as in case *b*, are the CaH bands ($^2\Pi$,$^2\Sigma$, $A/B = +19$) and the OH bands ($^2\Sigma$,$^2\Pi$, $A/B = -6.9$). The green MgH bands ($^2\Pi$,$^2\Sigma$, $A/B = +6$) are so near case *b* that only six branches have been found, although if the R_{21} and P_{12} branches could be detected, the bands would be of the eight-branch type.

The relations between the forms of the branches in $^2\Pi$(case *a*),$^2\Sigma$ and those in case *b* $^2\Pi$,$^2\Sigma$ bands can best be seen by comparing Fig. 29 with Fig. 30*a*, and Fig. 30*a* with Fig. 30*d*. Comparing Fig. 29 with Fig. 30*a*, the most important changes to be noted are the approach of the satellite branches to the main branches, and the pairing off of the main branches R_1 and R_2, Q_1 and Q_2, P_1 and P_2 for high J values. Comparing Fig. 30*a* with Fig. 30*d*, we note how the symmetrical contraction of the intervals $R_2 - R_1$, $Q_2 - Q_1$ and $P_2 - P_1$ and the fading out of the branches with double subscripts takes us over to the six-branch case *b* type. This in turn differs only slightly from the three-branch case *b′* type (cf. Figs. 25 and 19).

If we should draw median curves $\overline{P}$, $\overline{Q}$, and $\overline{R}$ in Fig. 30*a*, corresponding to averages of P_1 and P_2, Q_1 and Q_2, R_1 and R_2, these would have almost exactly the forms of the single P, Q, and R branches of case *b′* (same as the singlet band $^1\Pi$,$^1\Sigma$ of Fig. 19). This property of the median curves is maintained throughout the series of cases shown in Fig. 30. The $^SR_{21}$ and $^OP_{12}$ branches in Fig. 30*a* have approximately the form that S and O branches ($\Delta K = +2$) would have in case b' if they were possible there.

3a. *Special relations near case b for $A>0$.* We have now to consider some special relations which exist for small positive A/B values. First we may note that, as A/B is decreased from large values, case b conditions are reached at $A/B=4$, except for the $^2\Pi_{\frac{1}{2}}$ level $T'(\frac{1}{2})$ and the lines coming from this level. As A/B goes from 4 to 0, there is then at first a departure, especially in the forms of the branches for the lowest J values, from case b conditions toward case a, reaching a maximum for $A/B=2$ (examples, $^2\Sigma^-,^2\Pi$ λ3900 and $^2\Sigma^+,^2\Pi$ λ3143 bands of CH),[91] then again an approach to case b, this time for all levels and lines (example, BeH bands). The forms of the branches for $A/B=4$, 2, and 0 are shown in Fig. 30*b*, *c*, *d*. The arrangement of the energy levels should be examined at the same time (cf. MgH, CH, and BeH in Fig. 15). The intensity relations, except for a few of the lowest-numbered lines, are practically those of case b for the entire range of A/B values from -2 or less to $+6$ or more.

3b. *Spin doublet separations.* The doublet separations, $R_1(K)-R_2(K)$, Q_1-Q_2, and P_1-P_2 are determined, for all values of A/B in the $^2\Pi$ state, by the algebraic difference[101] of the doublet separations of the upper ($^2\Pi$) and lower ($^2\Sigma$) electron levels. For example,

$$R_1(K) - R_2(K) = [T_{1d}'(J' = K' + \tfrac{1}{2}) - T_{2d}'(J' = K' - \tfrac{1}{2})]$$
$$- [T_1''(J'' = K'' + \tfrac{1}{2}) - T_2''(J'' = K'' - \tfrac{1}{2})].$$

We know (cf. Eq. 36 of Part II*b*, as revised[55]) that the doublet separations of the $^2\Pi$ state are given by $T_1\alpha'(K)-T_2\alpha'(K)=\Delta\psi(K')+\gamma'(K'+\frac{1}{2})$, where $\alpha=c$ or d, those of the $^2\Sigma$ state by $\gamma''(K''+\frac{1}{2})$. The doublet separation $\Delta\nu_{12}$ for any branch (i.e. R_1-R_2 or Q_1-Q_2 or P_1-P_2) is then given by

$$\Delta\nu_{12} = \Delta\psi(K') + \gamma'(K' + \tfrac{1}{2}) - \gamma''(K'' + \tfrac{1}{2}). \tag{85}$$

Now $\Delta\psi(K')$, which strictly speaking differs slightly for the c and d sets of levels, is always negative except for A/B_v between 0 and $+4$ (cf. Fig. 15), but always approaches zero with increasing K as case b is approached. Normally, then, $\Delta\nu_{12}$ is negative, and, if γ' and γ'' are both approximately zero, $\Delta\nu_{12} \sim\Delta\psi(K')$, so that the behavior of the doublet separations $\Delta\psi(K')$ of the $^2\Pi$ levels can be read directly from the observed doublet separations $\Delta\nu_{12}$ in the P, Q, and R branches. In other cases, the $\Delta\nu_{12}$'s must first be corrected, especially for large K values, to get the $\Delta\psi$'s. When $\gamma'-\gamma''<0$, and $A/B_v<0$ or $>+4$, $|\Delta\nu_{12}|$ goes to a minimum with increasing K, then increases again. In the green MgH bands[90] we have a similar case: $\Delta\nu_{12}$ approaches approximately a constant value. With $A/B_v<0$ or $>+4$ and $\gamma'-\gamma''>0$, $\Delta\nu_{12}$ finally passes through zero and becomes positive with increasing K (example, red CaH bands, shown in Fig. 30*a* but with the $\Delta\nu_{12}$'s *greatly exaggerated.*)[90]

If instead of using the separations $^PQ_{12}-P_1$ etc. as in Eqs. (77) or P_1-P_2 etc. as in Eqs. (85), we take differences such as $^PQ_{12}(K)-P_2(K)$, we get directly

---

[101] This is the arithmetic *sum* in the usual case, where $T_2(K)>T_1(K)$ in the $^2\Pi$ but $T_1(K)>T_2(K)$ in the $^2\Sigma$ doublets.

the doublet separations $T_1\alpha'(K')-T_2\alpha'(K')$ of the $^2\Pi$ state. Thus (cf. e.g. Fig. 25 or 29)

$$^PQ_{12}(K'+1)-P_2(K'+1)=R_1(K'-1)-{}^RQ_{21}(K'-1)$$
$$=\Delta\psi_d(K')+\gamma'(K'+\tfrac{1}{2})\quad(85a)$$

$$^QR_{12}(K)-Q_2(K)=Q_1(K)-{}^QP_{21}(K)=\Delta\psi_c(K')+\gamma'(K'+\tfrac{1}{2})\quad(85b)$$

A discussion of spin doublet separations in a $^2\Delta,^2\Pi$ band near case *b* is given in section 4a.

4. *Other bands.* A few additional examples of multiplet bands other than $^2\Pi,^2\Sigma$ and $^2\Sigma,^2\Pi$ and involving intermediate coupling cases between *a* and *b* will now be treated briefly.

4a. $^2\Delta,^2\Pi$ *bands. Spin and* Λ*-type doublets near case b.* The $^2\Delta,^2\Pi$ CH band near λ4300 (cf. Figs. 26 and 27),[91] has already been discussed (cf. sections *I*5 and *I*7) as an example in most respects of case *b*. The $^2\Delta$ state is good case *b* down to the lowest *J* values, but the $^2\Pi$ state, with $A/B_v=+2$, belongs for low *J* values to an interesting intermediate case (cf. section *J*3a), so that the band merits further consideration in the present section. In such a band there are four main branches of each of the classes *P*, *Q*, and *R*. In the branches of each class, we can form two sorts of doublet separations $\Delta\nu_{12}$ and $\Delta\nu_{cd}$, e.g., in the *P* branches,

$$\Delta\nu_{12}=P_{1\alpha}(K)-P_{2\alpha}(K);\ \Delta\nu_{cd}=P_{idc}(J)-P_{icd}(J)$$

Here α stands either for *dc*, or for *cd*, in the case of *P* and *R* branches, and for *d*, or for *c*, in the *Q* branches, while $i=1$, or $i=2$. From Eq. (32) of Part II*b* and the revised[55] Eqs. (33) and (36), and the definitions of the branches (cf. Fig. 26), we obtain

$$\Delta\nu_{12}=\Delta\psi(K')-\Delta\psi(K'')+\gamma'(K'+\tfrac{1}{2})-\gamma''(K''+\tfrac{1}{2})\quad(86)$$

$$\Delta\nu_{dc}=[\phi_d(K',J')-\phi_c(K',J')]\pm[\phi_d(K'',J'')-\phi_c(K'',J'')].\quad(87)$$

The + and − signs in Eq. (87) respectively refer to the *P* and *R* and to the *Q* branches.

In the $^2\Delta,^2\Pi$ band of CH, $\Delta\psi(K')$, γ', and γ'' are small, so that the doublet separations $\Delta\nu_{12}$ taken directly from the band lines give approximately the quantity $-\Delta\psi(K'')=\psi_2(K'')-\psi_1(K'')$. Since $\phi_d(K',J')-\phi_c(K',J')\sim 0$ for $^2\Delta$ levels, the doublet separations $\Delta\nu_{dc}$ in the *P* and *R* branches, or $-\Delta\nu_{dc}$ in the *Q* branches, represent accurately the term doublet separations $\phi_d(J'')-\phi_c(J'')$. The band lines in CH λ4300 show in an interesting way (cf. Fig. 27) how the spin doublet widths $\Delta\psi(K'')$ are large for small *K* values but approach zero as *K* increases, while the Λ-type doublets $\phi_d(J'')-\phi_c(J'')$,—cf. section *I*7,—behave in the reverse manner.

The $^2\Delta$ state in the CH bands is interesting in that the $\Delta\psi$'s are at first small and negative,[91] corresponding to a very small negative value of *A*, but become positive for larger *K'* values, corresponding to a positive γ' (cf. Eq. (33) of Part II*b*, p. 107).

The $^2\Delta,^2\Pi$ band of SiH near λ4100,[102] which in terms of electronic configurations is doubtless the analogue of the CH band just discussed, shows interesting points of difference in respect to band structure. These result from the fact that A/B_v is much larger (about 20) for the $^2\Pi$ state than in the case of CH. The $^2\Delta$ state of SiH has a very small value of A like CH, although here it is positive.

In this SiH band, case b intensity relations are approximately fulfilled. But since the $^2\Pi$ state is nearly case a for low J values, while the $^2\Delta$ state is case b, the conditions correspond fairly well for low J values to the "mixed case" of section $J1$, and there is a distinct tendency for the development of all the twenty-four branches which fulfill the rule $\Delta J=0, \pm 1$. The relations are like those in the mixed case of a $^2\Pi$(case a),$^2\Sigma$(case b) transition (section $J2$), except that the number of branches is doubled because of the existence of Λ-type doubling in both initial and final states. The twelve case b main branches (cf. Fig. 26, full lines) are strong in SiH as in CH, but the eight case b satellite branches (cf. Fig. 26, dashed lines), which are only very fragmentarily detected in CH, and the four branches $^SR_{2d1c}$, $^SR_{2c1d}$, $^OP_{1d2c}$, and $^OP_{1c2d}$, which are forbidden in case b and not found in CH, are also present.[103]

4b. $^2\Pi,^2\Pi$ *bands.* The NO β bands are an example of a $^2\Pi,^2\Pi$ transition with case a conditions for low J values, but, especially rapidly for the upper $^2\Pi$ level, a change toward case b for higher J values.[104] This shows itself mainly in the forms of the branches. In the intensity relations there is no important change with J, since both initial and final states are intermediate between cases a and b, corresponding fairly well to the true "intermediate case" of section $J1$. The corresponding $^2\Pi,^2\Pi$ bands of O_2^+, on the other hand, according to preliminary results of Mr. D. S. Stevens in this laboratory, are probably an example of the "mixed case" of section $J1$, with a case b upper $^2\Pi$ and a case a lower $^2\Pi$ level. They show intensity relations quite different from those in the NO β bands.

4c. *Triplet bands.* In $^3\Pi,^3\Sigma$ and $^3\Sigma,^3\Pi$ bands relations analogous to those in $^2\Pi,^2\Sigma$ and $^2\Sigma,^2\Pi$ bands are expected. In the "mixed case" of $^3\Pi$(case a),$^3\Sigma$ bands, for example, nine P, nine Q, and nine R branches are expected, three of each for each of the three sub-bands $^3\Pi_0,^3\Sigma$, $^3\Pi_1,^3\Sigma$, and $^3\Pi_2,^3\Sigma$. Of these twenty-seven branches, eight would disappear if $A \rightarrow 0$ in the $^3\Pi$ state, ten would become weak satellite branches, while nine strong main branches would remain. The nature of the various branches is indicated in Fig. 31. The NH bands near λ3400 and the analogous PH bands[104a] are examples of $^3\Pi,^3\Sigma$ transitions with an (inverted) $^3\Pi$ state which is near case a for low J values but, rather rapidly in NH, goes over to case b with increasing J.

---

[102] C. V. Jackson, Proc. Roy. Soc. **126A**, 373 (1930). Although Jackson concluded that the $^2\Pi$ state is inverted, it has been possible to show that it is regular (R. S. Mulliken, forthcoming Phys. Rev.).

[103] Presumably all these are present, although only R_{2d1c}, R_{2c1d} (case b forbidden), Q_{21c} and Q_{21d} (case b satellites) were identified.

[104] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. **30**, 150–188 (1927).

[104a] R. W. B. Pearse, Proc. Roy. Soc. **129A**, 328 (1930).

The Swan bands of C_2 and the second positive bands of N_2 are well-known examples of $^3\Pi,^3\Pi$ bands.[105] The relations in these bands are probably like those in Fig. 34*b*. The N_2 bands are perhaps nearly case *a* even for fairly large J values, but the Swan bands, while showing case *a* characteristics for low J values, rapidly approach case *b* with increasing J. In both the Swan and the N_2 bands, the relation $A' \sim A''$ appears to hold, so that the transition from case *a* to case *b* proceeds for initial and final states at about the same

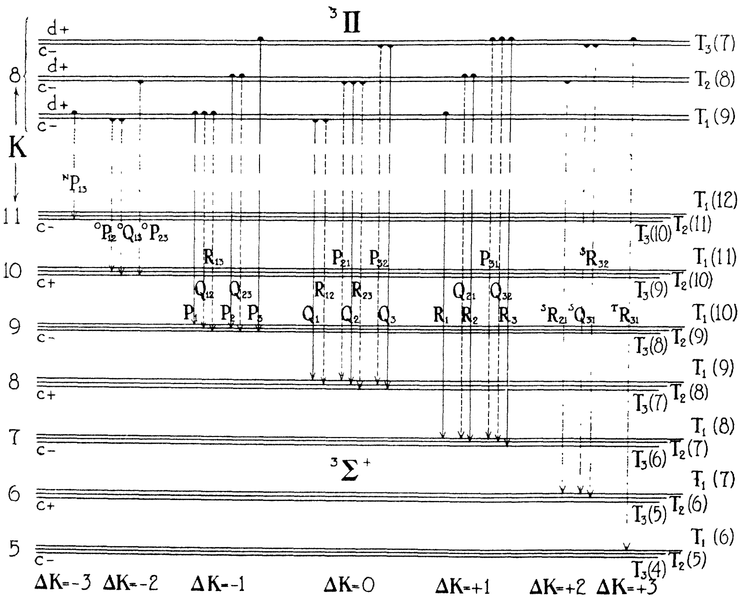


Fig. 31. Schematic diagram (not to scale) showing relations of possible band-lines to energy levels in a $^3\Pi \rightarrow {}^3\Sigma$ band. Only the levels corresponding (in case *b*) to a single K value are shown for the $^3\Pi$ state, and only one line of each possible branch is shown.

If the three $^3\Pi$ levels $T_1(9)$, $T_2(8)$, and $T_2(7)$ are close together (case *b*), only the nine main branches ($\Delta K=0, \pm 1, \Delta J=\Delta K$), shown by full lines, are strong. The ten satellite branches ($\Delta K=0, \pm 1, \Delta J=0, \pm 1$, but $\Delta J \neq \Delta K$) are very weak (except for very small J values) especially in the case of those where ΔJ and ΔK differ by two units. The remaining eight branches ($\Delta J=0, \pm 1$, but $\Delta K=\pm 2, \pm 3$) are practically absent, especially those with $\Delta K=\pm 3$, vanishing altogether if $A \rightarrow 0$ in the $^3\Pi$ state. If the three $^3\Pi$ levels are very widely separated (case *a*), all the branches should be present in considerable intensity. In all cases, the intensity relation $Q_i > R_i > P_i$ is to be expected, where the subscript i indicates that branches of similar type should be compared.

---

[105] Cf. R. S. Mulliken, Phys. Rev. **29**, 644 (1927) and **33**, 509 (1929).

[106] In $^3\Pi$(case *a*), $^3\Pi$(case *a*) one expects three strong P, three strong R, two weak Q branches (all with Λ-type doubling), and no others (cf. Eqs. 54–5). For $^3\Pi$(case *b*), $^3\Pi$(case *b*), one expects three main P and three main R branches, three weak Q main branches, and ten very weak satellite branches (cf. Eqs. 72), all with Λ-type doubling. Eight more branches fulfilling $\Delta J=0, \pm 1$ but violating $\Delta K=0, \pm 1$, all with Λ-type doubling, are to be expected in "mixed" coupling cases. But these and the satellite branches are to be expected only in negligible intensity in "intermediate cases" as here.

rate, and we have probably a good example of the "intermediate case" whose intensity relations have been discussed in section *J*1. As a result, there are are always only six strong branches, three *P* and three *R*, each with Λ-type doubling (cf. Fig. 34*b*).[106]

5. *Λ-type doubling in intermediate cases between a and b.* In multiplet states with $\Lambda > 0$, we have in case *b* (cf. section *I*7) Λ-type doublet widths which are independent of the orientation of *S* with respect to *K*, i.e. the doublet widths are the same for all *J* values associated with a single *K* value. In case *a*, however (cf. section *G*3), the Λ-type doublet widths are very different for different multiplet components. In intermediate cases, intermediate relations are obviously to be expected, and are found experimentally.

In $^2\Pi$ levels some interesting relations have been observed. According to to the theory as developed by Van Vleck, the Λ-type doublets in $^2\Pi_{1\frac{1}{2}}$ levels, which are very narrow in case *a*, should steadily widen in going toward case *b*. In the $^2\Pi_{\frac{1}{2}}$ levels the doublet widths, which are very large in case *a* with large $|A|$, should become smaller and *pass through zero* before case *b* is reached, so that the *c* and *d* levels reverse their energy order in going from case *a* to case *b* (cf. Fig. 16 of Part II*b*). Experimentally we cannot well verify this prediction by altering *A* in a molecule, but we can expect to do so by studying the variation of the Λ-type doublet widths with *J* for electron states which approximate case *a* for small *J* values and case *b* for large *J* values. The predicted behavior is verified in three examples of this sort, namely in the inverted $^2\Pi$ of OH ($A/B = -7.5$) and in the regular $^2\Pi$ states of SiH ($A/B = +20$) and of CaH ($A/B = +19$).[90,102] In the $^2\Pi_{\frac{1}{2}}$ levels the Λ-type doublet widths first increase with *J*, but soon get smaller again, pass through zero, and again increase, while in the $^2\Pi_{1\frac{1}{2}}$ levels the separations increase from the beginning.

K. BANDS OF MOLECULES COMPOSED OF TWO ATOMS OF THE SAME ELEMENT

1. *Even and odd electron states.* Molecules composed of two atoms both of the same element have a greater symmetry than other diatomic molecules, and this gives rise to characteristic new features in spectroscopic behavior. Before discussing the bands of such molecules, it is necessary to consider some properties of their energy levels.

In molecules with two equal atoms, every electronic state has the property of being either "even" or "odd." We shall designate even and odd states respectively by means of the subscripts *g* and *u* (German *gerade* and *ungerade*). These subscripts need not, however, be added unless the odd or even property is of importance for the discussion in hand. Examples: $^1\Sigma^+_g$, $^1\Sigma^-_u$, $^1\Sigma^+_u$, $^1\Pi_g$, $^1\Pi_u$, $^2\Pi_g$. In multiplet states, the even or odd character is the same for all components of a given multiplet. A case *a* $^2\Pi_g$ state, for example, comprises a $^2\Pi_{\frac{1}{2}g}$ and a $^2\Pi_{1\frac{1}{2}g}$ sub-level.

The meaning of "odd" and "even" electronic states can be understood only in terms of the quantum mechanics. The words odd and even really describe a property of the wave-function ψ_{el} of the molecule with nuclei assumed held fixed (cf. Part II, pp. 84–5). (ψ_{el} is the "electronic factor" of the complete wave-function ψ of the molecule.) Let the line joining the nuclei be taken as the z axis and the mid-point of this line as the origin. Which direction along the z axis is called positive does not matter. Then ψ_{el} is a function of x, y and z such that in symmetrical molecules $|\psi_{el}|$ always has exactly the same value for any point $(+x, +y, +z)$ as for the corresponding point $(-x, -y, -z)$. But ψ_{el} may either be the same (these are the *even* electronic states) or may change sign (*odd* states) when one exchanges $(+x, +y, +z)$ for $(-x, -y, -z)$.

These properties hold strictly only for a molecule composed of two identical atoms, such as H_2 or $(Cl^{37})_2$. But they also hold for all practical purposes for a molecule composed of any two atoms of the same element, e.g., $Cl^{35}Cl^{37}$, since the symmetry of the electric forces in the molecule, and of ψ_{el}, are not appreciably disturbed when one isotope is substituted for another.[107] Even in molecules composed of two atoms of two different elements nearly alike in atomic number, e.g., CN or better TlPb, ψ_{el} should be more or less approximately odd or even.

If the two nuclei of a (rotationless) symmetrical molecule could be pushed together until they were united, the even and odd states of the molecule would respectively become even and odd states of the atom. Even and odd states of an atom are those for which the sum Σl_r of the l_r values of the individual electrons is even or odd respectively. In atoms, there is a selection rule that *even states can combine spectroscopically only with odd states* and vice versa. A corresponding rule holds for the even and odd states of symmetrical molecules. This rule applies to molecules like $Cl^{35}Cl^{37}$ as well as to those like $(Cl^{37})_2$. In molecules like CN or TlPb, transitions between nearly-even and nearly-odd states should on the whole be much stronger than those between two states of like approximate symmetry.

2. *Rotational levels symmetrical and antisymmetrical in the nuclei.* In molecules composed of two *identical* atoms, i.e., of two atoms with nuclei of the same charge and mass and in the same quantum state (*homonuclear* diatomic molecules), every rotational level, or more accurately, its complete wave-function ψ, has the property of being "symmetrical" or "antisymmetrical" in the nuclei. In the following we shall find it convenient to resolve ψ into factors:[108] $\psi = \psi_{el}\psi_{rot}\psi_{nu}$. ψ_{el} has already been mentioned, ψ_{rot} corresponds to the rotation of the molecule, ψ_{nu} depends on the internal angular momenta of

---

[107] This symmetry of ψ_{el} is also usually not appreciably disturbed even when the nuclei are no longer regarded as fixed, and even if the motions of the two nuclei are unsymmetrical with respect to the geometrical center of the system. For the distribution of the electrons around the two nuclei, hence ψ_{el}, may usually be expected to adjust itself continuously and almost instantaneously to the varying positions of the nuclei. (For highly excited electron states, however, this is no longer possible.)

A consequence of this adjustment is that molecules like Cl^{35} Cl^{37}, just as much as those like $(Cl^{37})_2$, should maintain a zero dipole moment even when they vibrate, and so should have no vibration-rotation bands.

[108] Strictly, this resolution into factors is possible only for an assumed molecular model somewhat different from the real molecule, but for our purposes the results are the same as if a rigorous division were possible (cf. Ref. 110).

the nuclei of the two atoms. Whether any given level is symmetrical (Sy) or antisymmetrical (An) depends jointly on three elements, (1) the g or u character of ψ_{el}, (2) the $+$ or $-$ character (cf. section $C1$) of the rotational level, and (3) the symmetrical (s) or antisymmetrical (a) character of the factor ψ_{nu}.[109] If element (3) is s then the complete ψ is Sy if elements (1) and (2) are g, $+$ or u, $-$, but An if they are g, $-$ or u, $+$. If element (3) is a the results are reversed.[110] In symbols,

$$\begin{gathered}(g)(+)(s) = (u)(-)(s) = (g)(-)(a) = (u)(+)(a) = Sy; \\ (g)(+)(a) = (u)(-)(a) = (g)(-)(s) = (u)(+)(s) = An.\end{gathered} \tag{88}$$

[Some authors apply "symmetrical" and "antisymmetrical" (which when so used here, will be denoted S and A) to $\psi_{el}\psi_{nu}$: $g+ = u- = S$; $g- = u+ = A$.]

It is now recognized that the nuclei of atoms possess quantized angular momenta. Their values are indicated by a quantum number I, where $I^*h/2\pi$ is the angular momentum. I appears to have half-integral or integral values according as the number of protons in the atomic nucleus is odd or even, regardless of the number of electrons.[111] Often $I=0$, and in this case ψ_{nu} is necessarily s, since it is unaffected by exchanging the nuclei. When $I>0$, the function ψ_{nu}, which of course applies to the *two* nuclei regarded as one system, takes a variety of forms. These may be taken to correspond to the different possible orientations which the I^* vectors of the two nuclei can assume in an external magnetic field. A majority of the so-defined forms is always s and a minority a. The numbers of s and of a forms for each of several values of I are given in Table VI.[110]

TABLE VI. *Alternating intensity factors for homonuclear molecules.*

I	0	½	1	1½	2	2½	3	3½	4	4½
s	1	3	6	10	15	21	28	36	45	55
a	0	1	3	6	10	15	21	28	36	45

The band spectra of homonuclear molecules show features which are simply explained by the assumption that, for any given molecular species, only those rotational levels are capable of physical existence whose complete

---

[109] The symbols Sy and s really refer to the same property. Similarly with An and a. Slightly different symbols are, however, used here for the two cases of the complete ψ and of ψ_{nu}, for the sake of increased clarity in the discussion.

[110] For further details, cf. R. S. Mulliken, Trans. Far. Soc. **25**, Part 11, pp. 634–45 (1929). In this article, the existence of Σ^- in addition to Σ^+ states was unfortunately not recognized, so that the discussion needs in some places to be corrected.

[111] If a nucleus of atomic number Z contains P protons and E electrons, then $Z=P-E$. Usually E is even, and P and Z are both odd or even together. In all such cases known, I is half integral or integral according as Z (and P) are odd or even. But in the N^{14} nucleus, where $P=14$, $E=7$, it is found that $I=1$ (cf. Table VII). Also in the Cd isotopes (Z = even), some (presumably those with even P and E) appear to have $I=0$, others (presumably those with odd P and E) to have $I=\frac{1}{2}$. (Cf. review by Pauling and Goudsmit, Structure of Line Spectra, p. 222; but also C. L. Albright, Phys. Rev. **36**, 847 (1930), who casts doubt on the interpretation of the Cd hyperfine structures which leads to the two values $I=0$ and $\frac{1}{2}$). These facts are most simply explained by assuming that the proton spins (presumably all with $i=\frac{1}{2}$), but not the electron spins, contribute to I. Orbital angular momenta may also be present in the nucleus, but probably affect I only by integral amounts.

ψ is *Sy*, if the number of protons in each nucleus is even, or whose complete ψ is *An*, if the number of protons in each nucleus is odd.[112] This exclusion of half the conceivable states is analogous to the Pauli exclusion principle for electrons.

When $I=0$, the requirement just stated excludes half the rotational levels of every electronic state completely from physical existence. For when $I=0$, ψ_{nu} can take on only one (an *s*) form. Hence for an *even* electronic state, as-

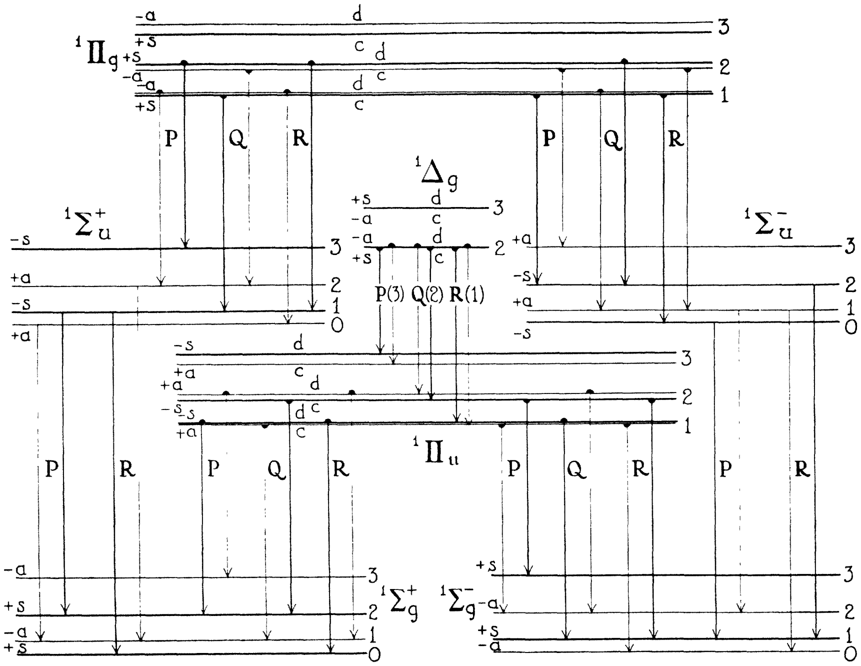


Fig. 32. Rotational levels and lowest-quantum-number transitions for several kinds of singlet states of a homonuclear molecule (cf. Fig. 17). All four of the possible types of $^1\Sigma$ states are shown, as well as all of the possible types of combinations of these (except that additional types can be obtained by exchanging the upper and lower electron levels in each case) with one another and with the two possible types of $^1\Pi$ states. The possible combinations $^1\Pi_g$, $^1\Pi_u$ and $^1\Pi_u$, $^1\Pi_g$ are not shown.

"Strong" levels and strong band lines are indicated by heavy horizontal and vertical lines in the diagram, "weak" levels and lines (missing if $I=0$) are shown by light lines in the figure. The indicated strong and weak levels and lines are correct on the assumption that the complete ψ is *Sy*. If, however, the complete ψ should be *An*, the interpretations of the heavy and light lines, and the designations *a* and *s*, in the diagram should be reversed. In any case, the strong levels are *s* and the weak levels *a*.

[112] It was at first supposed on theoretical grounds that only the *Sy* or the *An* levels would be found capable of existence according as the *total number* of particles (protons *and electrons*) in the nucleus is even or odd (cf. R. S. Mulliken, *l. c.*, Ref. 110). But Rasetti's work on the Raman spectrum of N_2 (cf. Zeits. f. Physik **61**, 598, 1930), where each nucleus contains 14 protons and 7 electrons, shows that only the *Sy* levels are present. This is presumably because there is an even number of protons and in spite of the fact that the total number of particles in each nucleus is odd.

suming that the complete ψ has to be Sy,[113] only *positive* rotational levels are allowed (g, $+$, $s = Sy$), for an odd electron state only negative levels (u, $-$, $s = Sy$). Figs. 32 and 34 show, for various types of electronic states, which rotational levels should be present (heavy lines) and which absent (light lines).

The bands of a homonuclear molecule with $I = 0$ are in structure and intensity relations exactly like those for the same kind of electron transition in an ordinary molecule, except that every other line is missing ("alternate missing lines"). Why this is true will be obvious from a study of the examples in Figs. 32 and 34*a*, and a comparison with those of Figs. 17 and 24. Which lines are present and which missing depends on the even or odd characters of the two electron levels involved, in a way which can be seen from Figs. 32 and 34. It will be seen that the number of distinct types or patterns of bands is greater than in ordinary molecules. The various possible types of $^1\Sigma, ^1\Sigma$; $^1\Pi, ^1\Sigma$, and $^1\Delta, ^1\Pi$ bands for a homonuclear molecule are shown in Fig. 33.

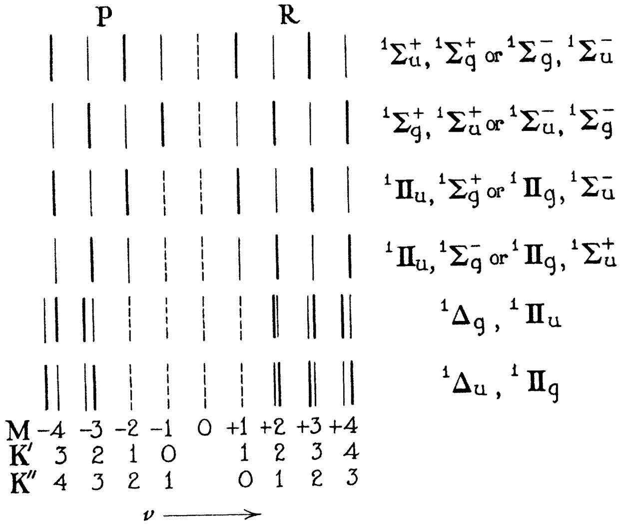
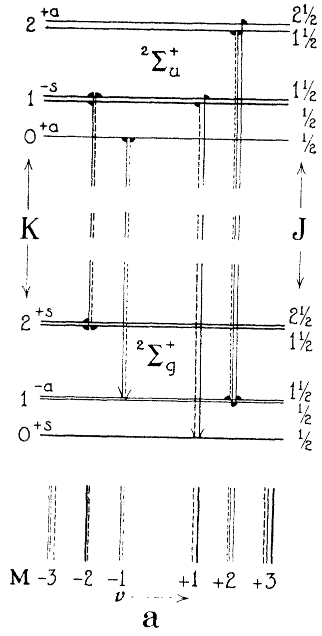


Fig. 33. Schematic diagrams of some band types for homonuclear molecules (cf. Fig. 18 for heteronuclear molecules). $B' = B''$ is assumed. In the case of $^1\Delta, ^1\Pi$ transitions, negligible Λ-type doubling is assumed for the $^1\Delta$ levels, and for the $^1\Pi$ levels it is assumed that the *d* rotational levels are above the *c* levels as in Fig. 32. Intensity relations in the bands are not indicated, except that "strong" lines are shown by heavy lines, "weak" lines (missing if $I = 0$) by light lines. This relation is true on the assumption that the complete ψ is Sy; if it should be An, the interpretations of the heavy and light lines must be reversed. The other intensity relations if shown would be like those in Fig. 18.

When $I > 0$, ψ_{nu} has some *s* forms and some *a* forms. Hence all the rotational levels of the molecule are possible, as in an ordinary heteronuclear molecule. Suppose for example that the complete ψ has to be Sy. (This is true[113]

---

[113] It is probable that $I = 0$ occurs only when the number of protons is even (cf. Ref. **111**), and it is also probable that the complete ψ must always be Sy when the number of protons is even (cf. Ref. 112).



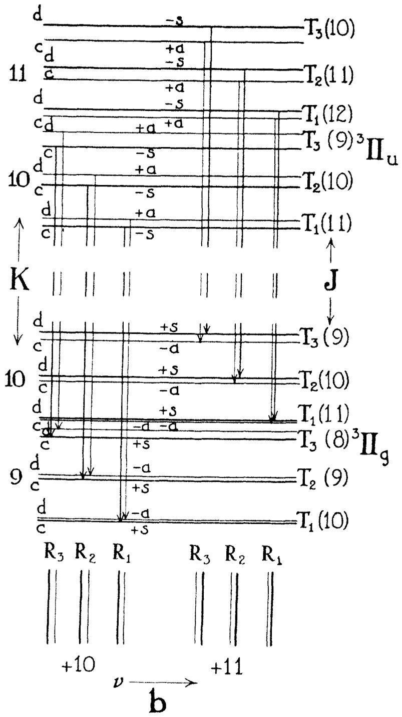


Fig. 34a. Lowest rotational levels and band lines for a $^2\Sigma^+_u$, $^2\Sigma^+_g$ transition of a homonuclear molecule, as an example of alternating intensities in case *b*. Strong levels and lines are shown by heavy lines, weak ones by light lines. The complete ψ is assumed *Sy*. $B'=B''$ is assumed. Cf. Fig. 24 for designations of band lines and relative intensities of lines (aside from the alternation ratio factor).

Fig. 34*b*. This figure shows a few rotational levels of a $^3\Pi_g$ and a $^3\Pi_u$ state of a homonuclear molecule, with strong and weak levels (heavy and light horizontal lines) drawn on the assumption that the complete ψ is *Sy*. The relative widths of the Λ-type doublets correspond, for both $^3\Pi$ electron levels, to *inverted* $^3\Pi$ (cf. last paragraph of this caption), and to coupling intermediate between case *a* and case *b*. $B'=B''$ is assumed. The Λ-type doublet widths are all exaggerated.

In case *a* (cf. Fig. 22) and with inverted $^3\Pi$, the Λ-type doublets would have practically zero width for the T_1 levels $(J=K+1)$, a moderate width proportional to $J(J+1)$ for the T_2 levels $(J=K)$, and a constant width for the T_3 levels $(J=K-1)$. In case *b* the rotational levels would all have Λ-type doublets of moderate width proportional to $K(K+1)$, the same for T_1, T_2, and T_3 (cf. section *I7*). From analogy to the $^2\Pi$ case (cf. Fig. 16 of Part II*b*) it seems possible that the order of the levels *c* and *d* reverses, for one or more of the sets of terms T_1, T_2, and T_3, (most probably in the series T_3, which becomes $^3\Pi_0$), in the transition from case *b* to case *a*. If such a reversal occurs, the order and spacings of Λ-type doublet levels would generally differ in intermediate cases from those shown in Fig. 34*b*. Unfortunately neither theory nor experimental data are yet available to show whether such a reversal really occurs.

The figure shows the arrangements and Λ-type doubling of two lines of each of the *main R* branches (R_1, R_2, and R_3) corresponding to transitions between the two $^3\Pi$ states. Expected very weak satellite branches (cf. Ref. 106) are not shown. The horizontal ν scale is greatly exaggerated compared with the vertical scale, except for the Λ-type doublets. In the band-lines of any series, alternately the left-hand and the right-hand component is weak (or missing if $I=0$). If the Λ-type doublets are imperfectly resolved, or if $I=0$, the members of any branch thus appear displaced alternately toward the left and toward the right from positions which would give a smooth series. For case *a* inverted $^3\Pi$ states, the R_1 lines, however, would appear single and undisplaced, because of the vanishing Λ-type doublet widths in the $T_1(^3\Pi_2)$ levels. Fig. 34*b* is fairly typical for a $^3\Pi$, $^3\Pi$ transition, but a great many variations are possible in respect to quantitative relations, including sign as well as magnitude of Λ-type doubling.

Everything in Fig. 34*b* would be just the same for regular $^3\Pi$ levels except that the Λ-type doublet widths would probably be constant in case *a* for the T_1 levels, which go to $^3\Pi_0$ in regular case *a*, and least for the T_3 levels, which go to $^3\Pi_2$. [But cf. second paragraph of the caption of Fig. 34*b*.]

if the number of protons in the nucleus is even.) Let us consider for definiteness a $^1\Sigma^+_g$ electron state. For $K=0, 2, 4, \cdots$ we have positive rotational levels, for $K=1, 3, 5, \cdots$ we have negative levels (cf. section *C*2). For the positive levels, since the electron state is *g*, we can fulfil the condition that the complete ψ shall be *Sy* by using any of the ψ_{nu} forms which are *s*, since $g, +, s = Sy$. For the negative levels we can also fulfil it, but this time by using any of the ψ_{nu} forms which are *a*, since $g, -, a = Sy$. Each rotational level can in general be realized in several ways, corresponding to different *s* or *a* forms of the function ψ_{nu}, but this does not result in any (measurable) splitting up or displacement of the energy level.

The statistical weights of the levels are, however, affected. The statistical weight of any level is in fact proportional to the number of different forms of ψ_{nu}, as given in Table VI, with which it may be realized, and at the same time of course to $(2J+1)$ as in ordinary heteronuclear molecules. Any series of rotational levels may be divided into two classes, differing in statistical weight, "*strong*" levels and "*weak*" levels. The strong levels are those for which ψ_{nu} is *s*, the weak levels are those for which it is *a*, since the number of *s* forms of ψ_{nu} is greater than the number of *a* forms, for every value of *I*. In every series of levels, the levels are alternately strong and weak. For instance in the example mentioned above of a $^1\Sigma^+_g$ state of a molecule whose complete ψ has to be *Sy*, the levels $K=0, 2, 4, \cdots$ which make use of the *s* forms of ψ_{nu}, are strong levels, while $K=1, 3, 5, \cdots$ having *a* forms of ψ_{nu}, are weak levels.

The bands of homonuclear molecules with $I>0$ show lines which are alternately strong and weak in each series ("alternating intensities"). Figs. 32–34 apply just as well to the cases $I>0$ as to $I=0$ if the heavy horizontal and vertical lines in the figure are interpreted as representing the strong energy levels and band lines, and the light lines as representing the weak levels and lines. The relations for $I=0$ really represent only an extreme case of those which exist for $I>0$.

Mention of some examples of actual bands corresponding to Figs. 32–34 may be of interest. Many of the types of Fig. 32, and some others, as well as corresponding case *b′* triplet bands, are found with alternate missing lines $(I=0)$ in the He_2 bands. The Swan bands of C_2 (cf. also section *J*4) are similar to the $^3\Pi$, $^3\Pi$ bands of Fig. 34*b*, with alternate lines missing $(I=0)$.[105] C_2 also has corresponding $^1\Pi$, $^1\Pi$ bands. The second positive N_2 bands are also $^3\Pi$, $^3\Pi$ bands similar to those of Fig. 34*b*, but nearer case *a* and also differing from Fig. 34*b* in that the $^3\Pi$ levels are regular, so that the R_3 (and P_3) lines appear single (cf. next to last sentence in caption of Fig. 34*b*).[105] The R_1,

R_2, P_1, and P_2 lines show alternating intensities ($I=1$). The N_2^+ bands are $^2\Sigma^+_u$, $^2\Sigma^+_g$ bands with alternating intensities ($I=1$), and correspond exactly to Fig. 34*a*, except in quantitative details. Many other examples could be cited.

3. *Alternating intensities and the determination of nuclear angular momenta.* The "alternation-ratio" AR in bands of homonuclear molecules may be defined as the ratio of the intensity of the strong lines to that of the weak lines under normal conditions, after due allowance has been made for the normal variation with J of the i and R factors of Eqs. (53). This ratio is approximately equal to the ratio of the intensity of any typical strong line to the average of the intensities of its two neighboring weak lines (one on either side). Theoretically this ratio is given by the ratio of the numbers of s and a states in Table VI. Thus for $I=0$, $AR=\infty$, for $I=\frac{1}{2}$, $AR=3$, for $I=1$, $AR=2$, and so on; for $I=\infty$, $AR=1$. In general, $AR=(I+1)/I$. Experimental measurements of this ratio from band spectra are important in that they give a means of determining I. They are, however, experimentally difficult, especially for the larger I values, where AR approaches 1. An independent method of determining I values exists in the analysis of hyperfine structures in line spectra. A list of I values determined from band spectra is given in Table VII. The table also gives the symmetry character (Sy or An) of the complete ψ for several molecules.[112]

4. *Selection rules in homonuclear molecules, for radiation and for collisions.* In homonuclear molecules, as we have seen, there is a selection rule $g\rightleftarrows u$ for electronic states in addition to the rule $+\rightleftarrows-$ which holds for the rotational levels of all molecules. Probably these rules are strict only for the dipole radiation of a molecule, but do not apply to its (very much weaker) quadrupole radiation.[114] The rule $Sy\rightleftarrows Sy$, or $An\rightleftarrows An$, however, is absolutely strict.[115]

From the three selection rules $+\rightleftarrows-$, $g\rightleftarrows u$, and $Sy\rightleftarrows Sy$ (or $An\rightleftarrows An$), there follows a fourth, nearly but not absolutely strict, selection rule concerning ψ_{nu}, namely that only $s\rightleftarrows s$, and $a\rightleftarrows a$, transitions are possible (cf. Figs. 32 and 34). This rule also appears to have independent validity. In fact, a broader rule can be given, namely that transitions very rarely occur, either spectroscopically *or in collisions*, in which the orientations (relative and absolute) of the angular momentum vectors of the two nuclei change. The reason for this rule is that the interactions (exclusively magnetic)of the two nuclear angular momenta with each other, or with the electrons, and with other molecules, are usually excessively small. Hence the nuclear angular momentum vectors are practically independent of one another and are also practically unaffected by what happens to the rest of the molecule, so long as it remains a molecule. The peculiar behavior of H_2 at low temperature, in which the level $K=1$ of the normal state, an s level, fails to revert to $K=0$, an a

---

[114] In regard to quadrupole radiation in atomic spectra, cf. A. Rubincowicz, Zeits. f. Physik **53,** 267 (1929); **61,** 338 (1930); **65,** 662 (1930); J. H. Bartlett, Jr., Phys. Rev. **34,** 1247 (1929); R. Frerichs and J. S. Campbell, Phys. Rev. **36,** 151 (1930); L. D. Huff and W. V. Houston, Phys. Rev. **36,** 842 (1930).

[115] Cf. W. Heisenberg, Zeits. f. Physik **41,** 261 (1927).

level, even when statistical equilibrium demands it, illustrates this rule. Another example is found in the "resonance spectrum" of the iodine molecule. Here the molecule is first excited to a single rotational level of a definite vibrational state by absorption of monochromatic light. Under some conditions the rotational quantum number J of the excited molecule is changed by collisions before the molecule radiates. But in all cases J changes in such collisions only by an *even* number of units, as is necessary if we are to have

TABLE VII. *I values from band spectra.*

N	P	E	Atomic species	Exptl. alt. ratio AR	I value (band sp.)	I value from at. spectra	Symm. of ψ	Evidence from spectrum of diat. molecule for stated symm. of ψ
1	1	0	H^1	3	$\frac{1}{2}$	—	*An*	Normal state ${}^1\Sigma^+_g$, levels with even K weak
2	4	2	He^4	∞	0	0	*Sy*	Lowest stable state ${}^3\Sigma^+_u$, levels with even K missing
3	7	4	Li^7	1.78	$1\frac{1}{2}$	$1\frac{1}{2}$ (or $\frac{1}{2}$?)	*An*	Normal state ${}^1\Sigma^+_g$, levels with even K weak
6	12	6	C^{12}	∞	0	—	[*Sy*]	
7	14	7	N^{14}	2.0(N_2^+)	1	—	*Sy*	Normal state ${}^1\Sigma^+_g$, levels with odd K weak
8	16	8	O^{16}	∞	0	—	*Sy*	Normal state ${}^3\Sigma^-_g$, levels with even K missing
9	19	10	F^{19}	at least 3, but not ∞	$\frac{1}{2}$	—	[*An*]	
11	23	12	Na^{23}	∽1	large (prob. at least 5/2)	1?	[*An*]	No alternation detected.
16	32	16	S^{32}	∞	0	—	*Sy*	Same as for O^{16}
17	35	18	Cl^{35}	1.36	5/2	—	*An*	Normal state ${}^1\Sigma^+_g$, levels with even K weak
53	127	74	I^{127}	∽1	large	—	[*An*]	No alternation detected

Notes for Table VII: N = atomic number; P = number of protons in nucleus (judging from atomic weight); E = number of electrons in nucleus ($E=P-N$); cf. Ref. 111. For references in regard to which levels are strong and which weak, and as to the experimental values of AR, cf. references cited on p. 643 of Ref. 110; also, for Li_2, A. Harvey and F. A. Jenkins, Phys. Rev. **35**, 789 (1930); for N_2, F. Rasetti, Zeits. f. Physik. **61**, 598 (1930); for Cl_2, A. Elliott, Proc. Roy. Soc. **127A**, 638 (1930); Dissertation Utrecht, 1930; for S_2, S. M. Naudé and A. Christy, Phys. Rev. 1931. In regard to the I value of Li^7 from the atomic spectrum, cf. L. P. Granath, Phys. Rev. **36**, 1018 (1930). The symmetry of the complete ψ given in the next to the last column is based on experimental evidence given in the last column, except when it is given in brackets. The evidence given in the last column is conclusive only if the correctness of the states given (${}^1\Sigma^+_g$ etc.) is assumed. In most cases this is practically certain, although based on theoretical considerations. In He_2, however, the odd character of the lowest stable state (${}^3\Sigma$) was first concluded from the absence of the even K levels and the *assumed Sy* character of the complete ψ; it is, however now supported by independent theoretical considerations, and so gives real evidence that ψ is *Sy*.

$s \rightleftarrows s$ and $a \rightleftarrows a$ (cf. Fig. 32), and in the resonance-collision bands alternate lines are missing, although this is not the case in the ordinary absorption bands.[110]

5. *Summary*. If we compare the band spectra of (*a*) molecules composed of atoms of two different elements, *e.g.*, HCl^{35}, (*b*) molecules composed of two isotopic atoms of the same element, *e.g.*, $Cl^{35}Cl^{37}$, (*c*) homonuclear molecules, *e.g.*, $(Cl^{35})_2$, we find the following likenesses and differences. Groups (*a*) and (*b*) show no alternating intensities, group (*c*) does. The electronic states of groups (*b*) and (*c*) have the property of being either even or odd (*g* or *u*), and spectroscopic combinations are limited to those between *g* and *u* states. Group (*a*) electron levels lack the *g*, *u* property and the corresponding selection rule. As a result, the observed spectra of group (*a*) molecules tend to be richer than those of similar molecules of group (*b*) or (*c*). For example, many more CO than N_2 band systems are known. Except for the differences mentioned, the bands of molecules composed of two atoms of the same element are essentially the same as those of other diatomic molecules.

The writer is indebted to Dr. Andrew Christy for valuable help in connection with the figures.