SEPTEMBER *PHYSICAL REVIEW* *VOLUME 28*

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. I. STATEMENT OF THE POSTULATES. INTERPRETATION OF CuH, CH, AND CO BAND-TYPES

BY ROBERT S. MULLIKEN

ABSTRACT

The problem of the interpretation of band-structure from combination relations; ambiguities and criteria for overcoming them. In the analysis of band spectra, it may often be assumed that each observed frequency is due to a combination of terms whose rotational energy parts are of the form $F(j)=Bm^2+\cdots=B(\sqrt{j^2-\sigma^2}-\rho)^2+\cdots$ (Kratzer-Kramers and Pauli term); here j is the quantum number corresponding to the total angular momentum, $mh/2\pi$ is the nuclear angular momentum, $\epsilon h/2\pi$ and $\sigma h/2\pi$ are electronic angular momentum components parallel and perpendicular to m, σ being also parallel to the internuclear axis. In the empirical analysis of band-structure in accordance with the combination principle, only *differences* such as $\Delta_1 F(j)=F(j+1)-F(j)$ and $\Delta_2 F(j)=F(j+1)-F(j-1)$ can be obtained. If derived from terms of the Kratzer-Kramers and Pauli type, these are (after expanding to remove the radical) of the forms $\Delta_1 F(j)=2B(T+\frac{1}{2})-B\rho\sigma^2/j(j+1)+\cdots$ and $\Delta_2 F(j)=4BT-2B\rho\sigma^2/(j^2-1)+\cdots$, where $T=j-\rho$ is defined as the **apparent or effective rotational quantum number.** Similarly, the most general expression (after expansion to remove the radical) for any band-branch is of the form $\nu=A+B'(\Delta T)^2+2B'T''\Delta T+(B'-B'')T''^2+f(j)+\cdots$; primes here refer to the more excited, double primes to the less excited state; $\Delta T=T'-T''$; $f(j)=(\rho'\sigma'^2/j'^2-\rho''\sigma''^2/j''^2)$. **P-form, Q-form, and R-form branches are defined** as branches for which $f(j)$ is zero and ΔT has the respective values -1,0 and $+1$; these are of the forms assumed by P,Q, and R branches ($\Delta j=-1,0,+1$) for the (usual) special case $\Delta T=\Delta j$. In case ρ and σ are simultaneously present and large enough so that the small $\rho\sigma^2$ term is experimentally detectable, the values of j, ρ, and σ can be determined directly if sufficiently accurate measurements are feasible. But in the usual case that one (or both) of the quantities ρ and σ are zero or nearly so, it is evidently impossible to determine j, ρ, and σ without the aid of additional information or assumptions, since the ΔF's and the forms of the branches are now functions of T' and T'' alone; in such cases it has ordinarily been tacitly assumed in the past, very often erroneously according to the present work, that $\sigma=0$. Criteria are discussed for overcoming these ambiguities of interpretation. These are (a) the presence or absence of Q branches (b) especially valuable, the absence of particular lines ("*missing lines*") near the band-origin, and finally (*c*) the postulates stated below.

Interpretation of bands of the CuH, HCl, CH, and CO types, and statement of the postulates. Recent work on the classification of electron levels in molecules in analogy with those of atoms is discussed; the NOγ bands (third positive nitrogen bands) are classified as $^2S\rightarrow{}^2P_{1,2}$, transitions and it is suggested that

Jevons' SnCl bands are due to the transition $^2S\rightarrow{}^2P_{1,2}$ in the Sn^+ ion in Sn^+Cl^-. The quantities ϵ and σ of the Kratzer-Kramers and Pauli formula are interpreted as components of an *electronic inner quantum number* j_e for the molecule as a whole, or in some cases as individual inner quantum numbers j_e for the two atoms of the molecule; in all cases it is found possible to assume that the j_e values for molecular states are identical with *Sommerfeld's j* values for corresponding atomic states.—Kratzer's interpretation of the violet CN bands($j=$ integral, $j_e=\rho\sim\pm\frac{1}{2}$ for both initial and final states) is adopted with slight modification; in addition, these bands are ascribed to a $^2S\rightarrow{}^2S$ transition, probably of a single outer electron. The same interpretation applies to a number of analogous band spectra, emitted by BO, CO^+, N_2^+, SiN, and AlO. The CuH, AgH, and AuH bands, and the infrared halogen halide bands, hitherto classed as essentially similar to the violet CN bands (all these bands have P- and R-form P and R branches only), are now interpreted as due to $^1S\rightarrow{}^1S$ electronic transitions, with j = half-integral, and $j_e=0$ for both initial and final states; the infrared CO bands probably have the same structure. This new interpretation makes understandable the single character of the lines in bands of the CuH type, as compared with the doublets of CN, and at the same time gives expression, in the j and j_e values, to the contrasting facts that CN contains an odd number of electrons, and molecules like CuH and HCl an even number. The importance of Kratzer's analysis of the CH bands ($j=$ integral, $\rho'=\pm\frac{1}{2}$, $\sigma'=0$, — the value of σ' represents a revision of Kratzer's $\sigma'=\frac{1}{2}$, — $\rho''=\pm\frac{1}{2}, \sigma''=1$) is emphasized. Since CH is an odd molecule like CN, the analysis confirms the possibility of $\rho=\pm\frac{1}{2}$ and of $j=$integral for odd molecules, which were *assumed* by Kratzer in the case of CN. The presence of Q branches may be attributed to the presence of σ''. The values $\rho''=\pm\frac{1}{2}$ and $\sigma''=1$ are respectively attributed to the H atom in its normal state and to the C atom in a ^1P excited state; the normal state of H is thereby classified as ^2S, as for the alkali metals, in confirmation of recent work in line spectra.—The observed structure of the CO Angstrom bands, including the presence of Q branches and the characteristic missing lines, is explained by the assumptions $j=$half integral (in accord with the assumptions made for CuH and other even molecules), $\rho'=0$, $\sigma'=0$, $\rho''=0$, $\sigma''=1$. The values of j_e here ($j_e'=0, j_e''=1$) are in complete agreement with Birge's interpretation of these bands, based on entirely different grounds, as $^1S\rightarrow{}^1P$.—With but slight generalization, the leading assumptions and conclusions involved in the above interpretations can be stated in the form of three simple postulates, which are stated on p. 503 (*q.v.*) and will not be repeated here. With the help of these postulates, a systematic interpretation of most known band spectra is possible. As a corollary of the postulates it is concluded that the normal state of all *diamagnetic gases* (H_2, N_2, CO, HCl, etc.) is probably a ^1S state ($j_e=0$); the paramagnetism of NO is attributed to its double ^2P normal state ($j_e=\sigma=\frac{1}{2}$ and $1\frac{1}{2}$), while that of O_2 is perhaps due to a ^3S normal state ($j_e=1$). An incidental result of the postulates is the disappearance of quarter-integral values of j and j_e.

INTRODUCTION

IN the development of the quantum theory of band spectra, the diatomic molecule was first treated as a simple rotator, then as a rotating harmonic oscillator, later as an anharmonic oscillator. Finally certain quantities ϵ and σ were introduced which are of the nature of electronic quantum numbers; and independently, evidence was found from other considerations for classifying various molecular electronic states in analogy to certain atomic states. It is with the correlation of these two last-mentioned phases of development, and the deduction of consequences from the results obtained, that the present series of papers is chiefly concerned.

The subject has already been discussed briefly in a preliminary paper.[1] Three postulates were there proposed which seem capable of accounting better than heretofore for many features of molecular spectra, and which also give results having a bearing on atomic spectra. The postulates were applied in a second paper[2] to the spectra of ZnH, CdH, and HgH. In the present paper, the empirical situation leading up to the formulation of the postulates is first discussed in more detail and from a somewhat different point of view. The postulates and some of their consequences are then presented and discussed. Definite interpretations (mostly different from those hitherto usual) are also given, in this and succeeding papers, for a large number of band spectra concerning which much uncertainty has existed, and in this way a very marked unification and systematization of the empirical side of the subject is obtained.

The first sections of the paper (up to p. 497) are devoted largely to a review of a number of empirical and theoretical relations which form a necessary foundation for the later discussion. Various new or hitherto insufficiently emphasized conclusions and relations are brought out; and at the same time a notation is set up.[3]

For a more general discussion of the quantum theory of band spectra reference should be made to Sommerfeld's "Atombau," 4th Edition,[4] and to a recent account by Kratzer,[5] or especially to the very complete treatment in the forthcoming National Research Council report.[3] Reference may also be made to several briefer reviews of the subject in which the empirical situation in regard to known band spectra is

---

[1] R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 144 (1926). The statements made on p. 144 of ref. 1 in regard to the occurrence of $\Delta j=0$, and on p. 145 in regard to three special cases of Q branches, are partially incorrect, and should be disregarded.

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

[3] The notation used is intended to conform as closely as possible to that adopted by the National Research Council Subcommittee on Radiation in Gases for their report on band spectra. It differs in one or two points (definitions of Δj and ΔT) from that used in refs. 1 and 2.

[4] A. Sommerfeld, "Atombau and Spektrallinien," 4th ed., chap. 9 (1924).

[5] A. Kratzer, Enzyklopedie der Math. Wissenschaften **5,** 821–59 (1925).

considered.[6,7,8] Reference should also be made to a brief review of a more theoretical nature by Kratzer.[9]

Matters related to the vibrational states of molecules and their changes will be largely subordinated in the present series of papers, since the correlations established are primarily between band-structure, which is qualitatively practically independent of the vibrational quantum number, and molecular electronic states.

QUANTUM THEORY OF BAND SPECTRA: ROTATIONAL ENERGY AND FINE STRUCTURE OF BANDS

Energy and spectroscopic terms of a molecule. For the rotating anharmonic oscillator, application of the quantum theory leads to the following familiar expression[4] for the energy contribution E^m due to rotation, m being the quantum number associated with the nuclear rotation, n the vibrational quantum number, and J the moment of inertia. Since in the analysis of spectra, wave-number units are ordinarily used, it will be convenient to use $F(m)=E^m/hc$ rather than E^m. Then:

$$F(m)=E^m/hc=[h/8\pi^2cJ_0-\alpha n]m^2-Dm^4+\cdots=Bm^2+\cdots \tag{1}$$

The total energy can be somewhat arbitrarily divided into (a)*electronic* energy E^e due to displacement of an electron from its normal orbit, (b) *vibrational* energy E^n, (c) *rotational* energy E^m. The term corresponding to the total energy of the molecule is then:

$$F=F(e)+F(n)+Bm^2+\cdots \tag{2}$$

Energy changes and band structure. In general, corresponding to a combination of two terms of the form of Eq. (2), there is an emitted frequency which can be written as follows:

$$\Delta F=\Delta F(e)+\Delta F(n)+\Delta F(m)=\nu^e+\nu^n+\nu^m=\nu^0+\nu^m=\nu. \tag{3}$$

All the bands emitted by a particular molecule and having a common value of ν^e (but differing values of ν^n and ν^m) are defined as a *band system.* Each different *band* corresponds to a different value of ν^n. In Eq. (3), ν^e often has more than one value for a single band-system, because of double or multiple electronic terms $F(e)$; these are analogous to multiplets in line spectra. The case $\nu^e=0$ corresponds to an infra-red oscillation-rotation band.

---

[6] R. Mecke, Phys. Zeit. **26,** 219 (1925). Especially valuable is the discussion of term-types and band-types, and the review of the experimental material.

[7] G. H. Dieke, Physica **4,** 193–218 (1924).

[8] R. Fortrat, J. de Phys. et le Radium **5,** 33 (1924).

[9] A. Kratzer, Naturwissenschaften **27,** 577 (1923).

In simple bands having $\Delta m = \pm 1$ (*e.g.*, the infra-red HCl bands), the equations for the lines of the two branches (respectively denoted the R and P branches) are of the form[4]:

$$\nu = \nu^0 + B' \pm 2B'm + Cm^2 + \cdots \qquad (C = B' - B''). \tag{4}$$

Here and in the following, *primes* attached to any symbol refer to a *higher*, *double primes* to a lower, energy level.

Kratzer's theory of rotational doublets of the violet CN *type*; *electronic quantum numbers*; *notation and combination rules for rotational terms of the violet CN type*. Empirically, the violet CN bands consist of a P and an R branch capable of being described by Eq. (4), using half-integral values of m, except for the fact that each line is split into a narrow doublet. This Kratzer explained[10,11] by assuming the existence of two slightly different rotational states for each value of m' and of m''. To account for this and the observed linear increase of the doublet separation with m (the doublets are unresolved near $m=0$), he proposed the following revision of Eq. (1):

$$F(j) = Bm^2 + \cdots = B(j \mp \epsilon)^2 \pm 2\delta(j \mp \epsilon) + \cdots \tag{5}$$

---

[10] A. Kratzer, Münch. Ber., p. 107 (1922), and later papers, in particular, Ann. der Physik **71,** 72 (1923).

[11] It is desirable here to attempt to justify Kratzer's *assumptions,* as embodied in Eqs. (6) and (7) and the relation $\epsilon' = \epsilon'' = \frac{1}{2}$. In the first place, Kratzer's rule $\Delta\rho = 0$ might conceivably be replaced[5] by $\Delta\rho = +1$ or -1 (e.g., $\rho' = +\frac{1}{2}, \rho'' = -\frac{1}{2}$, or $\rho' = -\frac{1}{2}$, $\rho'' = +\frac{1}{2}$). But it is easily shown that the two resulting P branches would be double-P-form and Q-form, respectively (cf. p. 492) and that the resulting R branches would be Q-form and double-R-form; and such branches are not observed.

A change of sign of ρ during emission would, however, seem more plausible for Q branches, since it occurs in the Q branches of bands of the HgH type.[2] As Dieke has shown (Zeits. f. Physik, **33,** 161, 1925; Physica, **5,** 178, 1925), Q branches of this type would in CN be exactly (due to $\epsilon'' = \frac{1}{2}$ exactly) superposed one on the observed P_1, the other on the observed R_2 branch. While the existence of such P-form and R-form Q branches here cannot be directly disproved, it makes no connection with a reasonable model, and also fails to account for the observed equality of intensity of the doublet components (P_1,P_2 and R_1,R_2). On the basis of Kratzer's interpretation, the latter can be explained very naturally as due to equality in the à priori probabilities of F_1 and F_2 states.

If other values of $\epsilon' = \epsilon''$ than approximately $\frac{1}{2}$ are used in Eqs. (6), other interpretations of the violet CN bands result. Birge has suggested (Phys. Rev. **25,** 240, 1925) what is in effect $\rho' = \pm 0.00115$, $\rho'' = 0$, $j =$ half integral; no explanation is given, however, of the double value of ρ'. The values $\epsilon' = \epsilon'' \sim 1$ or $1\frac{1}{2}$, etc., are also possible. The strongest argument against other values of ρ than $\frac{1}{2}$ is that the latter is the only value which fits into a unified picture with results on other band spectra. The assumption $\epsilon' - \epsilon'' = \pm 1$ would lead to results similar to those for $\rho' - \rho'' = \pm 1$, $\epsilon' = \epsilon'' = \frac{1}{2}$, and meets with similar objections.

Another possibility, instead of $\rho = \pm\epsilon$, would be that ρ possesses two slightly differing positive values both near $\frac{1}{2}$.

Here j (the notation here used differs from Kratzer's) is $2\pi/h$ times the *total* angular momentum of the molecule, and is assumed to differ by $\pm\epsilon$ from m, the quantity ϵ being of the nature of an electronic quantum number. The two signs of ϵ correspond to parallel and anti-parallel positions of ϵ with respect to m. By assigning integral values to j, setting $\epsilon=\frac{1}{2}$, and giving δ a very small positive value, two nearly coincident values of $F(m)$ are obtained for each value of m. These correspond to $(j+1)-\epsilon$ and $j+\epsilon$, and give an explanation of the observed double terms.

The presence of a linear term in j, as used by Kratzer, is open to theoretical objections.[12] $F(j)$ can equally well be represented without this term, if ϵ values differing slightly from $\frac{1}{2}$ are used. The values $\epsilon'=0.49885$ or 0.50115, $\epsilon''=0.500$, suffice to account for the observed doubling in the violet CN bands (for not too large values of m), according to calculations of Birge.[13] In the following this interpretation of the bands will be used.

To avoid confusion, the symbol ρ will be used to embrace both $+\epsilon$ and $-\epsilon$; thus $\epsilon=|\rho|$. It will frequently be necessary in the following to distinguish between terms where $\rho=+\epsilon$ and those where $\rho=-\epsilon$. In agreement with Kratzer, the former will be called F_1 terms, the latter F_2 terms, thus

$$\begin{aligned} F_1(j)&=Bm^2+\cdots=B(j-\epsilon)^2+\cdots; \\ F_2(j)&=Bm^2+\cdots=B(j+\epsilon)^2+\cdots \end{aligned} \tag{6}$$

According to Kratzer, the four observed branches in the violet CN bands are then interpreted (cf. Eq. (3)) as in Eq. (7). It is important to note that *P and R branches are here defined in terms of changes of j, not of m.*

$$\begin{aligned} R_1(j)&=\nu^0+F_1'(j+1)-F_1''(j)\,; \quad R_2(j)=\nu^0+F_2'(j+1)-F_2''(j) \\ P_1(j)&=\nu^0+F_1'(j-1)-F_1''(j)\,; \quad P_2(j)=\nu^0+F_2'(j-1)-F_2''(j) \end{aligned} \tag{7}$$

The doublets are formed by $R_1(j+1)$ and $R_2(j)$, and by $P_1(j+1)$ and $P_2(j)$. This is because, with $\epsilon'=$approximately $\frac{1}{2}$, $F_1'(j+1)$ and $F_2'(j)$, and likewise $F_1''(j+1)$ and $F_2''(j)$ if $\epsilon''=$nearly $\frac{1}{2}$, are nearly equal (cf. Eq. (6)). Thus, although the pair of values (j',j'') differs for the two components of a doublet, the pair (m', m'') is practically the same for the two components. If $\overline{R}(m)$ and $\overline{P}(m)$ denote *mean values* for the two components of each doublet, Eq. (4) is then applicable to $\overline{R}$ and $\overline{P}$.

---

[12] R. T. Birge, cf. E. C. Kemble, J.O.S. **12**, 4 (1926), footnote on p. 4.

[13] As shown by Birge (Phys. Rev. **25**, 240 (1925)) and Dieke (Physica **5**, 178, (1925)), there is an error in the δ values given by Kratzer. The ϵ' and ϵ'' values given above are the result of unpublished calculations of Professor Birge.

Empirically, the structure is the same (aside from the doublets) as if $\rho=0$, $j=m=$half-integral. For a more complete discussion, reference should be made to Kratzer's paper.[10,11]

It will be noted that, according to Eq. (7), combinations occur only between F_1' and F_1'', or F_2' and F_2'', but not between F_1' and F_2'' or F_2' and F_1'' terms. This is a rule which apparently always holds for P and R branches.

Electronic quantum numbers and the Kratzer-Kramers and Pauli formula for the rotational term. In his well-known 1919 paper, Lenz discussed the possibility of an electronic angular momentum (to which would correspond a quantum number which has more recently been designated by σ) around the figure axis, and deduced some of its consequences.[14] Kratzer,[9] and Kramers and Pauli,[15] later generalized this to include both a ρ and a σ (both assumed fixed in the molecule), as follows:

$$F(j)=Bm^2+\cdots=B(\sqrt{j^2-\sigma^2}-\rho)^2+\cdots \tag{8}$$

According to Kramers and Pauli, ρ in Eq. (8) should appear only with the positive sign, for reasons of dynamical stability; but Kratzer has shown that in various cases (*e.g.*, the CH bands and bands of the HgH type) the observed facts can be explained only by admitting $\rho=-\epsilon$ as well as $\rho=+\epsilon$, as in Eq. (6).

Four important special cases of Eq. (8) can conveniently be distinguished, as follows:

$$F(j)=B[(j-\rho)^2-\sigma^2+\rho\sigma^2/j+\ldots.]+\ldots\ldots \tag{8A}$$

$$F(j)=B(j-\rho)^2+\ldots. \tag{8B}$$

$$F(j)=B(j^2-\sigma^2)+\ldots. \tag{8C}$$

$$F(j)=Bj^2+\ldots. \tag{8D}$$

In the general case it is convenient to write Eq. (8) in the developed and expanded form of Eq. (8*A*), which represents a sufficient approximation except for the smallest values of j. An example involving case (8*B*) has just been discussed; examples involving the other cases, and the problem of distinguishing the various cases, will be considered below.

An important fact in Eqs. (6) and (8) is that it is not m, but j, which is quantized and which takes on a succession of integral or half-integral values. In fact, when σ is present the successive values of m are not even rational, and do not differ by integers.

---

[14] W. Lenz, Verhandlungen der Deutschen Phys. Ges. **21,** 632 (1919).

[15] H. A. Kramers and W. Pauli, Jr., Zeits. f. Physik **13,** 351 (1923).

Definition of j_e. It is convenient to have a symbol for the quantum number (if such it is) corresponding to the resultant electronic angular momentum of a molecule. This will now be denoted by j_e. In general, $j_e=\sqrt{\rho^2+\sigma^2}$, but in practice, either ρ or σ is usually approximately zero, and in known cases (e.g. CH and OH) where both ρ and σ are present, it proves to be more appropriate to speak of the molecule as having two j_e's, one for each atom. The necessity, which exists in the case of molecules, of distinguishing between j and j_e, obviously disappears in the case of atoms, but to minimize possible confusion, j_e rather than j will generally be used below in referring to atomic inner quantum numbers.

Definition of P, Q, and R branches. According to the correspondence principle,[4,9] the possible changes of j should be limited to $\Delta j=+1$ (R or positive branch),0 (Q or zero branch), and -1 (P or negative branch); here $\Delta j=j'-j''$. Frequently P, Q, and R branches are simultaneously possible, but for certain types of electronic transitions, one, or perhaps sometimes even two, of the three possible kinds of branches should be lacking.[9]

The significance of Q branches.[1] For oscillation-rotation band ($\nu^e=0$ in Eq. (3)), the presence of a σ is a necessary and sufficient condition for the presence of a Q branch.[4,9] In the case of electronic bands, the presence of a σ (either a σ' or a σ'' or both) appears to be a *sufficient* condition for the presence of a Q branch, for practically any reasonable type of motion of the emitting electron[16]; but it is *not*[15] a *necessary* condition. Conversely, when Q branches are lacking in an electronic band, we can be fairly sure that $\sigma'=\sigma''=0$, hence that the nuclear motion is a pure rotation. The *presence* of Q branches in an electronic band is on the other hand a strong indication, although not in general more than this, of the presence of a σ' or σ'' or both. In practise a σ' or σ'' seems always to be present when Q branches occur, and vice versa.

THE SIGNIFICANCE OF MISSING LINES

Terms of the σ type. The "missing lines" near the origin of a band should be of great value for the interpretation of band structure. In the case of rotational terms of the σ type (Eq. (8C)), the missing lines should

---

[16] If the motion of the emitting electron should happen to be a linear vibration along a line always perpendicular to both j and j_e, P and R branches should occur alone, even if a σ were present. But this case is very improbable.

[17] Cf. ref. 4, especially p. 745–46; it should, however, be noted that the H_2O and MgH_2 bands to which Sommerfeld makes reference are really in all probability OH and MgH bands.

be determined by the fact[14,15,17] that j cannot be less than σ (cf. Eq. (8)). This rule determines, for each homologous set of molecular terms, a minimum value of j, which will be denoted $j_{min.}$ The value of $j_{min.}$ should be that of the next integer or half-integer (according as the values of j are integral or half-integral,—cf. postulate III, p. 503) equal to or greater than σ. Thus $j_{min.}$ is of great value in setting close limits to σ, a quantity which for terms of the pure σ type (Eq. (8C)) is not otherwise open to experimental test (unless by such means as the Zeeman effect). The method of determination of $j'_{min.}$ and $j''_{min.}$ in practise is illustrated by the discussion of the CO bands (p. 501) and of bands of the HgH type.[2]

Terms of the ρ type. If $F(j)$ is of the ρ type (Eq. (8B)), there is some uncertainty as to the expected value of j_{min} for a given set of rotational terms. *For F_1 terms* (cf. Eq. (6)) $j=m+\epsilon$, and it seems fairly clear that the value of j_{min} should be that of the next integer or half-integer, as the case may be, equal to or greater than ϵ. *For F_2 terms*, where $j=m-\epsilon$, one would naturally expect j_{min} to have the smallest possible positive value, namely 0 or $\frac{1}{2}$, as the case may be. For both cases the relations just suggested can be considered as consequences of a *guiding principle* (or postulate) that for a *homologous series* of terms there should be at no point a reversal from a parallel to an anti-parallel orientation of m and ϵ: for it is precisely such a reversal which distinguishes the F_1 from the F_2 term-series.

Kratzer's exclusion of the state $j=0$. In his analysis of the violet CN and of the ZnH, CdH, and HgH bands,[10] Kratzer has arbitrarily excluded the state $j=0$ for both F_1 and F_2 terms. According to the principle of the preceding paragraph, the state $j=0$ is not possible for F_1 terms with $\epsilon=\frac{1}{2}$, but for F_2 terms it should be possible. In the last analysis, the *experimental* evidence for Kratzer's exclusion of $j=0$ for F_2 terms now consists[18] only in the probable absence of the line $R_2(0)$ in the HgH bands λ4017 and 4219; in the corresponding ZnH and CdH bands the evidence is inconclusive.[2] The line $R_2(0)$ would involve a state $F_2''(0)$; but if this is really absent, the fact might be attributed[2] to the presence of a σ'' in addition to ϵ''. In the violet CN bands (cf. Eq. (7)), the absence of $R_2(0)$ and $P_2(1)$, which respectively involve $F_2''(0)$ and $F'_2(0)$, has been *assumed* by Kratzer, but there is no experimental evidence[19] for (nor, perhaps, against) this assumption, since these lines cannot be

---

[18] The absence of lines such as $P_2(1)$ and $Q_2(0)$ in HgH was cited by Kratzer as evidence that $F_2'(0)$ must also be excluded arbitrarily. But this exclusion is now explained[2] as due to the presence of a σ'.

[19] In regard to possible evidence from intensity data, cf. R. T. Birge, Phys. Rev. **25**, 240 (1925) and G. H. Dieke, Zeits. f. Physik **33**, 161 (1925).

resolved from their respective doublet-companions $R_1(1)$ and $P_1(2)$. Finally, there is apparently conclusive direct evidence, in the data on the CH and OH bands, that the state $j=0$ actually occurs for F_2 terms; this evidence will be given in a later paper.

The null-line. The probable absence in HgH of $R_1(0)$, and the practically certain absence in the violet CN bands of the null-line, which corresponds to $R_1(0)$ plus $P_1(1)$, are adequately explained by the principle stated in the second preceding paragraph, since the lines mentioned would involve $F_1(0)$ terms.

Terms of the general Kramers and Pauli type. The values of $j_{min.}$ can be readily predicted here by an extension of the principles used above in the cases of ϵ-type and σ-type terms.

AMBIGUITIES IN THE CORRELATION OF EMPIRICAL AND THEORETICAL BAND STRUCTURES

Combination differences. In the analysis of band spectra, the application of the combination principle does not give directly $F(j)$, but only *differences* of this function. In practise, these are of two kinds. In bands having only P and R branches, and frequently also in other cases, the only type of difference that can be obtained is of the form[20]

$$\Delta_2F(j)=F(j+1)-F(j-1) \tag{10}$$

Such differences are obtained in bands of the violet CN type (cf. Eq. (7)) as indicated by Eq. (11), where $i=1$ or 2:

$$\Delta_2F_i'(j)=R_i(j)-P_i(j)\,; \quad \Delta_2F_i''(j)=R_i(j-1)-P_i(j+1) \tag{11}$$

In practise, the difference is formed between a particular pair of lines (one P and one R) suspected of having a common initial or final state, then between the next pair of lines, and so on. Similar differences are then formed in other bands of the same system. If the entire set of differences so formed for one band agrees, within the errors of measurement, with a corresponding set for another band having the same value of the final vibrational quantum number n'', these differences may be regarded as probably real $\Delta F''$'s. In case of accurate agreement for bands having the same n', the differences are probably real $\Delta F'$'s. To be rigorously certain of the reality of a set *either* of $\Delta F'$'s or of $\Delta F''$'s, it will be seen on close examination that it is necessary to obtain such quantitative agreements in the case of *both* sets.

---

[20] Of course $\Delta_2F(j)$ could alternatively be defined as $F(j+2)-F(j)$, but the form chosen is more convenient in practice.

When Q branches are present, additional combination relations frequently also exist from which differences of the following form can be obtained[6]:

$$\Delta_1 F(j) = F(j+1) - F(j). \tag{12}$$

These are obtained by appropriate combinations of P and Q, or of Q and R lines (cf. Eqs. (17) and (18)). They can be tested in the same way as the $\Delta_2 F$'s, but also, as will be seen from Eqs. (17) and (18), in another way requiring data only on a single band. The existence of combination relations can also be tested in various other ways which are often useful.[5]

Effective rotational quantum numbers. Setting $j-\rho=T$ in Eq. (8A), to give Eq. (8E), the following ΔF equations are readily obtained; in these equations the quantity T evidently plays an important part which is well described by calling it the "*effective rotational quantum number.*"

$$F(j) = Bm^2 + \cdots = BT^2 - B\sigma^2 + B\rho\sigma^2/j + \cdots \tag{8E}$$

$$\Delta_1 F(j) = 2B(T+\tfrac{1}{2}) - B\rho\sigma^2/j(j+1) + \cdots \tag{13}$$

$$\Delta_2 F(j) = 4BT - 2B\rho\sigma^2/(j^2-1) + \cdots \tag{14}$$

From Eqs. (13) and (14) it will be seen that from an observed set of ΔF's, absolute values of B, T, and T_{min} can be determined if good experimental data are available. One must of course first know whether the ΔF's are $\Delta_1 F$'s or $\Delta_2 F$'s, since otherwise B may be incorrectly evaluated and the T values be in error by a half unit; but there is seldom any difficulty on this score in practice. Empirically, T is usually *approximately* either an integer or a half-integer, or sometimes apparently a quarter-integer. It is important to note that in case $\sigma=0$, $T=m$; if $\epsilon=0$, $T=j$.

The empirical form of the ΔF's gives no information, however, in regard to the values of ρ, σ, j, and j_{min}, *unless* ρ *and* σ *are simultaneously present* and large enough so that the product $\rho\sigma^2$ is of appreciable magnitude (say perhaps $\epsilon\sigma^2 > 0.2$). In this comparatively infrequent special case, j, $j_{min.}$, ϵ and σ can be directly determined from the analysis, provided observations of sufficient accuracy can be made on lines corresponding to the lowest values of j.

Except in cases where there is experimental evidence of a $\rho\sigma^2$ term in ΔF, it has hitherto generally been tacitly assumed that $\sigma=0$. This, however, is evidently unjustified, since if $\rho \sim 0$, the possible presence of a σ in Eq. (8) or (8A) would be without effect in Eq. (13) or (14). Thus if T is found to have the values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, ... one cannot distinguish between the possibilities (1), j=integral, $\rho=\pm\frac{1}{2}$ (either with or without a *small* σ), and (2), j half-integral, with $\rho=0$, and $\sigma \geqq 0$.—The writer is greatly indebted in this matter to Professor E. C. Kemble, who first brought to his attention the indistinguishability of the ΔF's arising from terms of the forms of Eqs. (8B) and (8C).

P-, Q-, and R-form branches. Closely related to the question of effective rotational quantum numbers is that of the *form* of the branches of a band. For any band-line, $\nu=\nu^0+B'm'^2-B''m''^2+\ldots.$ (cf. Eqs. (2), (3), and (8)). Substituting for $B'm'^2+\ldots.$ and $B''m''^2+\ldots.$ according to Eq. (8E), reducing, and setting $T'-T''=\Delta T$, $\nu^0+B''\sigma''^2-B'\sigma'^2=A$, $B'-B''=C$,and $(\rho'\sigma'^2/j'-\rho''\sigma''^2/j''+\ldots.)=f(j)$, Eq. (15), which is a generalization of Eq. (4), results:

$$\nu=A+B'(\Delta T)^2+2B'T''\Delta T+CT''^2+f(j)+\ldots\ldots \qquad (15)$$

From the definitions of T and ΔT, $\Delta T=\Delta j+(\rho''-\rho')$. Eq. (15) contains the description of all possible branches which can occur by the combination of two terms for which $F(j)$ has the form of Eq. (8).

The simplest case, and the most common in practise, is that in which $\Delta T \sim \Delta j$ and $f(j)\sim 0$, corresponding to $\rho'\sim\rho''$ and $\rho'\sigma'^2\sim\rho''\sigma''^2\sim 0$, as in the violet CN bands ($\epsilon\sim\frac{1}{2}$), the CuH bands ($\rho\sim 0$, $\sigma=0$), or the CO bands ($\rho'=0, \sigma'=0; \rho''=0, \sigma''=1$). In this case the P, Q, and R branches ($\Delta j=-1$, 0, and $+1$, cf. p. 488) take on familiar characteristic forms. But in other cases other forms are assumed, *e.g.*, if $\rho'\sim 0$, $\rho''\sim\pm\frac{1}{2}$, as in the ZnH and analogous bands,[2,10] ΔT has the respective values $+1\frac{1}{2}$, $+\frac{1}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$, $-1\frac{1}{2}$, for the R_1, R_2, Q_1, Q_2, P_1 and P_2 branches. Such cases as P or R branches with $\Delta T=0$, or Q branches with $\Delta T=+1$ or -1, are also entirely possible. It is convenient to *define P-form, Q-form, and R-form branches* as branches for which $f(j)\sim 0$ and ΔT has approximately the respective values -1, 0, and $+1$. Branches corresponding to $\Delta T=+2$, $-1\frac{1}{2}$, $+\frac{1}{2}$, etc. (with $f(j)\sim 0$) may be referred to as double-R-form, $1\frac{1}{2}$-P-form, semi-R-form, etc.—In case $f(j)$ is appreciable, the forms of branches are essentially unchanged except for a characteristic deformation (cf. Eq. (15)) for the smallest values of j.

Methods of distinguishing ρ-type and σ-type terms. From the foregoing, it is obviously necessary to find other criteria than the mere form of the empirical ΔF's, or of the observed branches, in order to distinguish between rotational terms of the ρ and σ types (Eqs. (8B) and (8C)) and the Eq. (8D) type. This necessity is also clear from the fact that up to the present all bands not obviously containing terms of the form of Eq. (8A) have been tacitly *assumed* to involve only terms of the (8B) or (8D) form; while according to the present work, many of these same bands have been found to involve terms of the (8C) form.

Two valuable aids to decision have been discussed in the two preceding sections. If Q branches are lacking,[21] we can safely[16] rule out the $B(j^2-\sigma^2)$ type in favor of the $B(j-\rho)^2$ type of term. If they are present, we have a strong indication in favor of the $B(j^2-\sigma^2)$ type of term for at least one of the two electronic states. If this is correct, a study of the missing lines yields the value of σ;[22] in fact, the absence of one or more lines

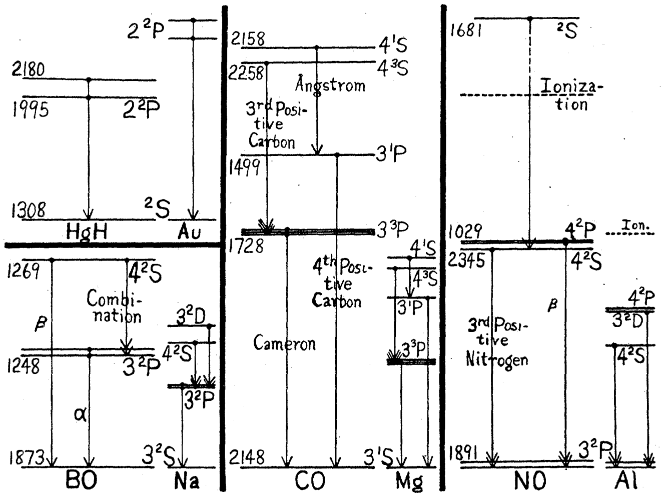

Fig. 1. The energy-levels are all on a uniform scale, except that the doublet separations have been exaggerated ten times in the case of the octet molecules and the correpsonding atoms,—but not in the cases of HgH and Au. The figures in parentheses are vibration frequencies ω_0, expressed in wave-number units, as determined from the band spectra. These give a rough indication of the stability of the molecule for the electronic state in question. At the right are term-designations, including tentative values of the principal quantum number. The energy levels of CO are as given by Birge,[24, 28, 34] complete energy level diagrams of CO, N_2, CO^+, N_2^+, NO, O_2, and O_2^+ are given in a recent article by Birge and Sponer.[34] In regard to BO, cf. ref. 31. The scheme of levels for NO is as determined by Sponer.[34,37] The term-designations are by the writer. The highest level in NO, since it lies above the ionization potential, probably involves simultaneous excitation of two electrons. Denoting by ($3s$, $3s$, $4s$) the individual states of the three outer electrons which give rise to the 4^2S state of NO, this higher state may well be another ^2S state (since experimentally it is single) corresponding to the arrangement ($3s$, $4s$, $4s$). The designation of the NO β bands as $^2P \rightarrow {}^2P$ is a result of recent unpublished work of Dr. F. A. Jenkins, Dr. H. A. Barton, and the writer.

---

[21] This of course assumes that one can distinguish true Q branches from true P or R branches, regardless of the form; the uncertainties here involved are illustrated in the discussion of the violet CN bands in ref. 11. There is also the difficulty that very short weak Q branches, such as are to be expected in certain cases (cf. discussion in later papers), are likely to be overlooked.

[22] This is strictly true only with the help of the assumption that σ must be either integral or half-integral.

having $T>\frac{1}{2}$, if one can be sure of it, is in itself satisfactory evidence for the presence of a σ.

Since the half-integral or integral character of $T=j-\rho$ can be determined experimentally, it is evident that if we had rules for determining whether j, ρ, and σ should be integral or half-integral for a particular molecule, the ambiguities above brought out might be practically eliminated. Precisely this function is fulfilled by the postulates stated below (p. 503).

RECENT WORK ON THE NATURE OF ELECTRON LEVELS IN BAND SPECTRA

It is natural to suppose that the electronic states of molecules have more or less similarity to those of atoms.[23] Much evidence can be obtained from a study of the electronic frequencies ν^e (cf. Eq. (3)) alone or with the help of analogies of band-structure between different spectra. The subject has recently been discussed by Birge[24] in an article which gave impetus to the present work.

The first, and very striking, evidence for a parallelism between molecular and atomic electron levels was the discovery of Rydberg series in the spectrum of He_2.[25] There is also evidence of similar series in the H_2 spectrum.[23,26] In the case of other molecules, the evidence is at present slight, although in several cases two or three members of a probable series are known.[24,27,28]

Term-designations. Beyond the establishment of Rydberg series, one might hope to assign definite term-designations and quantum numbers to the electronic states of molecules. After the failure of early attempts at simple molecular models, further efforts were, however, largely held in abeyance.

The first attempt to carry through a systematic analogy between atomic and molecular spectra was made by Mecke.[29] Mecke assumed that the angular momentum of the emitting electron and of the nuclei, in molecules, are respectively analogous, in determining multiplet structure, to the angular momentum of core and of emitting electron in atoms. But Mecke's treatment requires a molecular model[29] which seems

---

[23] Cf. ref. 4, pp. 92, 734 and 740.

[24] R. T. Birge, Nature, Feb. 27 (1926).

[25] A. Fowler, Proc. Roy. Soc. **91A,** 208 (1915); W. E. Curtis and R. A. Long, Proc. Roy. Soc. **108A,** 513 (1925). Cf. also R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 158 (1926).

[26] E. E. Witmer, Proc. Nat. Acad. Sci. **12,** 238 (1926).

[27] Excitation potentials of N_2, cf. H. Sponer, Zeits. f. Physik, **34,** 622 (1925).

[28] CO energy levels, R. T. Birge, Nature, Feb. 13 (1926).

[29] R. Mecke, Zeits. f. Physik **28,** 261 (1924) and **31,** 709 (1925).

very improbable for the cases to which he applies it, and is open to serious objection in other ways. The postulates stated below, and the conclusions reached, differ radically from Mecke's, although at some points there is a close superficial resemblance.

Recently evidence was presented by the writer,[30] for a real analogy between the electronic states of certain molecules (BO, CN) and those of the Na atom. These ideas were extended in a later paper which laid some of the foundations for the present work,[31] while additional important evidence has been put forward by Birge, Mecke, and Hulthén. Finally, Birge has postulated a more or less strict and literal analogy between molecular electronic states and certain corresponding atomic states.[24]

The above development has already been reviewed briefly.[1] Some of the results, together with certain new results, are discussed below and in part summarized in Fig. 1. Fig. 1 contains term-designations, including a tentative principal quantum number of the excited electron, for the observed electronic energy levels of three typical "octet molecules"[1] and of HgH, with comparison diagrams of certain comparable atoms. The term-notation is essentially that suggested for use in line spectra in the paper of Russell and Saunders.[32] It is especially important that each diagram in Fig. 1 is *typical* for molecules (neutral or ionized) having the same number of outer electrons. Thus, so far as the data go, the energy levels of CO^+, CN, and N_2^+ (also of SiN and AlO, with eight more electrons) are qualitatively identical[31] with those of BO; those of N_2 are like those of CO[24]; and in O_2^+ there is a system of double-headed ultraviolet bands[33,34,35] which evidently correspond to the β bands of NO. Certain new SiN bands recently described by the writer[36] are probably also of the same type, since in all obvious features they have the same structure as the NOβ and the O^{2+} bands.

Evidence for "octet" structure. The striking parallelism in *nature* (single or double) and *arrangement* of the electron levels in BO, CO, and NO (and their respective homologues) to those of the comparable atoms[24,31] Na, Mg, and Al is evident from Fig. 1. It is on this parallelism that the assigned term-designations and the idea of an "octet" structure for such molecules, plus one, two, or three (3-quantum) outer electrons, are chiefly based. The nature of this structure, and the evidence for it, are further discussed elsewhere.[1,24,31,38]

---

[30] R. S. Mulliken, Phys. Rev. **25**, 291 (1925).

[31] R. S. Mulliken, Phys. Rev. **26**, 561 (1925).

[32] H. N. Russell and F. A. Saunders, Astrophys. J. **61**, 64 (1925).

[33] R. C. Johnson, Proc. Roy. Soc. **105A**, 683 (1924).

[34] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[35] R. Mecke, Zeits. f. Physik. **36**, 795 (1926). The writer is indebted to Dr. Mecke for the opportunity to examine the manuscript before publication.

There is, however, evidence against the "octet" structure and in favor of a molecular model composed of two essentially unchanged atoms whose j_e's interact as seems to be the case in H_2, Na_2, etc.[38] Such a model is indicated by recent evidence of Birge and Sponer,[34] which shows that even such typical octet molecules as CO and NO can probably be dissociated into normal or only slightly excited atoms as the limit of a process of increasing the vibrational quantum number in the normal or one of the excited electronic states of the molecule. Also, Mecke has pointed out[35] that the doublet separations in BO, CO^+ and NO are of the same order of magnitude as the (triplet) separations for the normal state of the O atom, indicating that the emitting electron belongs to the O atom. In the writer's opinion, however, the relations brought out by Mecke are not necessarily incompatible with an octet structure, although the O atom may well exert a dominating influence on account of its relatively great nuclear charge.

Even if the octet idea should prove incorrect, there remains strong evidence, in octet as well as in other molecules (see below), for the existence of multiple electronic states which closely resemble those of atoms.

Other molecules. Aside from octet molecules, evidence has recently been produced from several sources for the existence of ^2P double electronic states. Thus it is likely that the doublet alkaline earth halide bands correspond to the resonance transition $^2P_{1,2} \rightarrow {}^2S$ in the Me^+ ion (*e.g.*, Ca^+) in diatomic molecules Me^+X^- of the one-valence-electron type.[30,39] Mecke has obtained some very interesting quantitative correlations between the observed doublet separations and those of certain corresponding atoms in ^2P states.[40]

The existence of a pair of excited P states in ZnH, CdH, and HgH, related to the P levels of Zn, Cd, and Hg, was first brought out by Hulthén, who supposed the two levels to be $^3P_1$ and $^3P_2$.[41] They have been interpreted as ^2P levels by Mecke[35] and the writer[2]; the doublet separations are close to those of the preceding monovalent atoms Cu, Ag, Au (cf. Fig. 1). Similar relations hold in the alkaline earth halides[40] and in SnCl.[42]

---

[36] R. S. Mulliken, Phys. Rev. **26,** 319 (1935); new bands, p. 334.

[37] H. Sponer, Nature, Jan. 16, 1926); H. Sponer and J. J. Hopfield, Phys. Rev. **27,** 640A (1926).

[38] R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 338 (1926).

[39] R. S. Mulliken, Phys. Rev. **26,** 31 (1925).

[40] R. Mecke, Naturwissenschaften, Sept. 4, 1925.

[41] E. Hulthén, Nature, October 31, 1925.

[42] W. Jevons, Proc. Roy. Soc. **110A,** 365 (1926).

An interesting further example occurs in a pair of band-systems described by Jevons, and due to SnCl.[42] Qualitatively, these show exactly the same relations (ω_0 greater for initial state, final electron level double, etc.) as for the $^2S \rightarrow {}^2P_{1,2}$ bands of NO. These bands are then probably due to the transition $^2S \rightarrow {}^2P_{1,2}$ in the Sn^+ ion in a Sn^+Cl^- molecule. The observed doublet separation $\Delta\nu$ is about the same as that of the normal state of the In atom which, like Al and NO, has three outer electrons, and which has the same total number of electrons as Sn^+.

Inapplicability of the azimuthal selection principle. In the cases of BO (cf. Fig. 1) and CO^+ there exist observed *intercombinatons of three electron levels*, and for at least one of these it would seem that there must be a definite failure to obey the azimuthal quantum selection principle of line spectra, *no matter what term-designations* (*including primed terms*) might be substituted for those given.[43]

PRELIMINARY CORRELATION OF BAND-STRUCTURE AND ELECTRONIC STATES IN TYPICAL BAND SPECTRA

In earlier sections the influence on band-structure of the quantities ρ and σ has been discussed. Various ambiguities in their experimental determination and criteria for overcoming these, have also been pointed out. It is now natural to try to correlate the evidence from band-structure with the results reviewed in the preceding section, in order to determine finally the real values of ρ and σ and to find how these correspond to S, P, D, etc., electronic states. Such a correlation is expressed in the three postulates stated in the next section and in various conclusions reached with their help. In the present section the postulates will be made plausible by a consideration of typical band spectra, and later will be tested and justified by application to a large number of other spectra. In connection with the present section, reference to the statement of the postulates (p. 503) may be helpful.

Spectra containing terms of the $B(j-\rho)^2$ *and* Bj^2 *types*; *comparison and interpretation of* CuH, HCl, *and violet* CN *band-types.* As has been hinted more than once already, Kratzer's interpretation of the violet CN bands comes near to being the key to the entire situation. It is very instructive

---

[43] The following facts should, however, be noted: the BO combination bands (Fig. 1) are notably weak (R. S. Mulliken, Phys. Rev. **25**, 284 and 291, 1925); and the CO^+ combination bands, while rather intense at high pressure, at low pressure become very weak compared with the other two systems (F. Baldet, Comptes Rendus **180**, 1201, 1925). It therefore seems possible that these "combination" bands occur only through a violation of the selection principle favored by external electric fields or the proximity of other molecules, and that the other two systems (Fig. 1) are "regular;" this was in fact the writer's original idea (Phys. Rev. l.c., p. 291) in regard to the BO combination bands.

to compare these bands with the electronic bands[29,44,45] of CuH and the infra-red oscillation-rotation bands of HCl. All three sets of bands are superficially almost identical in structure. All have *P*-form and *R*-form branches only, which we may without much risk assume to be real *P* and *R* branches (cf. ref. 11 on violet CN bands); we can then conclude[16] (cf. p. 498) that $\sigma'=\sigma''=0$ for all. All have half-integral values of T' and T'' (cf. p. 491-2), and in all $T'_{min.}=T''_{min.}=\frac{1}{2}$, since the only evidence of missing lines is in each case a single gap in the series at the null-line. But the lines of the violet CN bands consist of doublets, while those of the CuH bands, and, so far as is known, of the HCl bands, are single.[46,47] The existence and importance of this difference were first emphasized by Mecke.[29]

Analogous to Eqs. (7) and (11) for the violet CN bands, the following equations, which will be introduced here for convenience of later reference, may be expected to hold for the CuH and HCl bands, the only difference being that we are dealing here with single terms:

$$R(j)=F'(j+1)-F''(j)\,; \qquad P(j)=F'(j-1)-F''(j) \tag{16}$$

$$\Delta_2F'(j)=R(j)-P(j)\,; \qquad \Delta_2F''(j)=R(j-1)-P(j+1) \tag{17}$$

As already noted in an earlier section, Kratzer *assumed* integral j values for the violet CN bands, and then found that the observed doublets could be explained by setting $\rho'\sim\rho''\sim\pm\frac{1}{2}$. If integral j values are again assumed for HCl[15] and CuH, one again concludes $\epsilon'=\epsilon''=\frac{1}{2}$; but since the lines are single, only one sign of ρ can be used: either $\rho=+\frac{1}{2}$ or $\rho=-\frac{1}{2}$ seems admissible.[48] Except for the unexplained singleness of the lines, this explanation at first sight seems satisfactory.

But there is a difference between CN and the other two molecules which, if all these molecules were atoms, would be of fundamental importance: CN contains an odd number of electrons, while CuH and HCl each contain an even number. For atoms, this difference would involve a corresponding shift between integral and half-integral values of the inner quantum number j. Of course we may dismiss the matter with the

---

[44] CuH bands: R. Frerichs, Zeits. f. Physik **20**, 170 (1923); E. Bengttson, Zeits. f. Physik **20**, 229 (1923); absorption of CuH, AgH, AuH, and AlH bands, E. Hulthén and R. V. Zumstein, Phys. Rev. **28**, 13 (1926).

[45] Isotope effect in CuH bands, cf. R. S. Mulliken, Nature **113**, 489 (1924).

[46] In the case of HCl, there is, however, no real experimental evidence against the presence of unresolved narrow doublets.

[47] The direct evidence is very strong that the CuH lines are strictly single (except for a doubling due to isotopy).[29,45] Birge finds (Phys. Rev. **27**, 245A, 1926) that the T' (but not the T'') values depart quite appreciably from half-integers. This is enough practically to insure that doublets, if present, would be resolved.

[48] If one arbitrarily excludes $j=0$, with Kratzer, the case $\rho=-\frac{1}{2}$ is not in accord with observation, since it would give three central missing lines.

remark that molecules do not necessarily behave like atoms; but it seems more reasonable, in the absence of evidence to the contrary, to suppose that they *do* in such respects behave like atoms.

Furthermore, it is generally admitted that the HCl molecule must have an electron shell like that of the argon atom, while, as we have seen in the preceding section, there are strong reasons for believing that the CN molecule[49] has a single valence electron which gives rise to energy levels like those of a Na atom. Now in the HCl bands we are unquestionably dealing with the normal electronic state of the HCl molecule, which should then be a ^1S state like the normal state of argon. This conclusion is further supported by the fact that HCl, like argon, is diamagnetic. In the case of CN, as we have seen, there is strong evidence that the electron levels concerned in the emission of the violet CN bands are both ^2S levels. The lower of these is in all probability[49] the normal state of the molecule, the ^2S level here corresponding to that of the normal state of the Na atom. For a ^2S state $j=\frac{1}{2}$ according to Sommerfeld, $J=1$ according to Landé; for a ^1S state, $j=0$, $J=\frac{1}{2}$.

Everything now fits into place in a most significant way if we suppose that Sommerfeld's atomic j values are the correct j_e values (cf. p. 487) for molecules in corresponding electronic states. The adoption of $j'_e = j''_e = \rho' = \rho'' = \pm\frac{1}{2}$ (in agreement of course with Kratzer) for the violet CN bands, and $j'_e = j''_e = 0$ for the CuH and HCl bands, explains at once the double character of the P and R branches for CN, and their single character in the latter cases. Landé's J values, requiring $\rho = \pm 1$ for the violet CN bands, $\rho = \frac{1}{2}$ for the CuH and HCl bands, would not explain this difference, although apparently capable of explaining the other observed relations.

A consequence of the above interpretation is that for HCl and CuH, the j values are half-integral, while for CN they are integral. This can be seen from Eqs. (8D) and (14); since j_e, ρ, and σ are zero for CuH and HCl, we have $j = m = T = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$, for both initial and final electronic states. Denoting integers by τ, half-integers by τ^*, the results may be summarized thus: HCl, HCu, $(j_e, m, j) = (\tau, \tau^*, \tau^*)$; CN, $= (\tau^*, \tau^*, \tau)$.

[49] The direct evidence that the bands are really due to the molecule CN is very strong (cf. R. S. Mulliken, Nature **114**, 838, (1924). The evidence becomes conclusive when the complete analogy[31] of the violet CN bands to corresponding bands of a number of other emitters, in particular N_2^+, is recognized. Similar but slightly less positive statements hold in regard to the evidence that the final state of the violet CN bands is the normal state of the CN molecule; for the N_2^+ bands, the final state has been shown by resonance potential work[27] to be the normal state of N_2, thus showing by analogy that the same in all probability is true for CN.

According to the above interpretations, the absence of the null-line, both in the CN and the CuH bands, is to be explained as discussed on p. 490, and not in agreement with Kratzer. Kratzer's explanation of the missing null-line in the CN bands, as due to the arbitrary exclusion of the state $j=0$ (cf. p. 490), is obviously inapplicable to the CuH bands as here interpreted, since j is half-integral.

According to the above interpretation, the CuH bands correspond to an electronic transition ${}^1S \rightarrow {}^1S$.[50] As in the case of the ${}^2S \rightarrow {}^2S$ transitions (violet CN bands) in CN, we must conclude that the emitting electron is not subject to an azimuthal quantum selection principle, and also that the line spectrum prohibition against the change $0 \rightarrow 0$ of j_e is inapplicable here.

The preceding results can be extended to a number of additional band spectra. With the violet CN bands are to be classed the AlO, SiN, N_2^+, BO β, and CO^+ negative Deslandres bands (cf. p. 495); with the CuH bands the analogous AgH and AuH bands (including the new AuH bands of Hulthén and Zumstein[44]); and with the infra-red HCl bands the corresponding HF and HBr bands.

Spectra containing terms of the general Kramers and Pauli type; *the* CH *bands*. As already noted (p. 492), values of j, ρ, and σ can be determined without assumption in the case of bands involving terms of the form of Eq. (8) with both ϵ and σ of appreciable magnitude. The two CH bands λ3900 and λ4300, as analyzed by Kratzer,[51] have a common final state for which $F(j)$ is clearly of this type, with $\sigma''=1$, $\rho''=\pm\frac{1}{2}$, $j=$ integral. The values of $\Delta F(j)$ are, to be sure, not very sensitive to the exact values of σ and j, except for very small j values, but careful examination of all available data, especially for the λ3900 band, indicates that the above values are essentially correct. For the initial states[52] of λ3900 and λ4300, $\sigma=0$, $\rho=\pm\frac{1}{2}$.

The resulting band structure is highly complex but easily recognizable after the analysis into branches has been made. Especially characteristic is the presence of doublets[6] whose separation is small for large values of j but increases rapidly for small j values.[50] In λ 3900 there are two P, two Q, and two R branches, in λ4300 there are four branches of each kind.

---

[50] The possibility that one or both of the electronic states are ${}^3P_0$,—which like ${}^1S$ has $j_e=0$,—can safely be dismissed because if it were true there should also be ${}^3P_1$ and perhaps ${}^3P_2$ combinations.

[51] A. Kratzer, Zeits. f. Physik **23**, 298 (1924).

[52] For the *initial* state of the λ4300 band, Kratzer has tentatively concluded $\sigma=\frac{1}{2}$, $\rho=\pm\frac{1}{2}$, but both the writer and Professor R. T. Birge independently have become convinced that this result is incorrect and that actually $\sigma'=0$. For the initial state of λ3900, Kratzer's conclusion $\sigma=0$, $\rho=\pm\frac{1}{2}$, cannot be criticized.

The above results are important in a number of ways. (1) They show that the general Kratzer-Kramers and Pauli rotational term of Eq. (8) actually occurs in practise,[53] and that a σ really can exist; the presence of this σ, furthermore, accounts for the presence of the observed Q branches (cf. p. 488). (2) They confirm the assumption of integral j values for CH and therefore probably for all odd molecules. (3) They give evidence that a ρ can exist and have the values $\pm\frac{1}{2}$, and thus give support to Kratzer's interpretation of the violet CN bands. (4) The observed ϵ and σ values can reasonably be interpreted as $\sigma=1=j_e$ for the carbon atom, $\epsilon=\frac{1}{2}=j_e$ for the hydrogen atom; the fact that $\sqrt{\epsilon^2+\sigma^2}=1.12$ is neither an integer nor a half-integer is evidence that in the CH molecule there is no resultant molecular j_e, but that instead there are two uncombined atomic j_e's.[54] The value 1 (of σ) is exactly Sommerfeld's j_e for a carbon atom in a ^1P state, (probably not $^3P^1$). The value $j_e=\frac{1}{2}$ is exactly what Sommerfeld's j_e would be for the normal state of the H atom *if it acted like an alkali metal* atom, and may be considered evidence that it does act in this way; this result is in line with recent work of several writers.[55] (5) The evidence stated in (4) for Sommerfeld's j_e values gives support to their applicability in the cases of CN, CuH, HCl, and analogous molecules, and therefore (as will be seen by an examination of the discussion of these spectra) to the m and j values there deduced; the evidence of (2) also supports the j values for CN and its analogues.

Band types having rotational terms of the form $B(j^2-\sigma^2)$: CO *Angstrom bands*. In a recent paper[2] it was shown that the ZnH, CdH, and HgH bands can be more adequately interpreted than heretofore if their initial states involve rotational terms essentially of the form $B(j^2-\sigma^2)$, as in Eq. (8C). A simpler example will now be considered.

The visible CO bands ($^1S\rightarrow{}^1P$ transition in Fig. 1) of Angstrom and Thalén, as recently analyzed by Hulthén,[53] appear to be of the simplest possible type. They contain one P and one R branch, and have $T'=T''$

---

[53] The objection might be raised that the CH bands constitute an isolated case and that the agreement with the theoretical form is fortuitous, since in the closely analogous OH bands the agreement with the simple formula is only qualitative. But the peculiarities of the OH bands can be explained fairly simply by the assumption of a σ and ϵ which vary systematically with j, a circumstance which may be attributed to an appreciable departure from the rigid fixation of j_e which is assumed by Kramers and Pauli in deducing Eq. (8).

[54] Of course if $\sigma=\sqrt{3/4}=0.87$, we should have $\sqrt{\epsilon^2+\sigma^2=1}$, and it is barely possible that $\sigma=0.87$ is within the limits of error.

[55] S. Goudsmit and G. E. Uhlenbeck, Physica **5,** 266 (1925); J. C. Slater, Proc. Nat. Acad. Sci., Dec., 1924; A. Sommerfeld and A. Unsöld, Zeits. f. Physik **36,** 259 (1926).

[56] E. Hulthén, Ann. der Physik **71,** 41 (1923); Dissertation Lund, 1923. Cf. also Mlle. O. Jasse, Comptes Rendus **182,** 692 (1926).

=half-integral, exactly as in the CuH bands, but in addition possess a Q branch.

The following assumptions are now very natural: (*a*) CO, being an even molecule, has half-integral j values like CuH and HCl; (*b*) the initial state of the Angstrom bands has $j_e=0$ like the ^1S (initial and final) electronic states of CuH and HCl; (*c*) the final state of the Angstrom bands has $j_e=1$, corresponding to Sommerfeld's j for a ^1P state, and this appears in the form $\sigma=1$, $\rho=0$. A little consideration shows that these assumptions are in complete accord with the observed T values, and also account for the presence of the Q branch. According to assumptions (*b*) and (*c*), the initial rotational term is of the simple form $F'(j)=Bj^2$, the final term of the form $F''(j)=B''(j^2-\sigma^2)=B''(j^2-1)$; and in *both* cases (cf. Eqs. (12) and (13)) $\Delta_1 F$ is of the form $\Delta_1 F=2B(j+\frac{1}{2})$. In agreement with this, taking into account assumption (*a*), the empirical ΔF's are both of the form $\Delta_1 F=2B\tau(\tau=\text{integral})$.

The above assumptions involve very definite requirements as to missing lines (cf. p. 488–89), and thus permit a critical test of their correctness. Since $F'(j)=Bj^2$, we may expect j' to have the values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, . . .; but for j'' we can expect only $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, ... , since $F''(j)=B(j^2-1)$. The first possible lines in the P, Q, and R branches, respectively, should then correspond to the following transitions $(j'\rightarrow j'')$: $P(\frac{1}{2}\rightarrow 1\frac{1}{2})$, $Q(1\frac{1}{2}\rightarrow 1\frac{1}{2})$, $R(2\frac{1}{2}\rightarrow 1\frac{1}{2})$. The lines $Q(\frac{1}{2}\rightarrow\frac{1}{2})$ and $R(1\frac{1}{2}\rightarrow\frac{1}{2})$, the latter of which is present in HCl and CuH, should thus be cut out. The above-predicted lines are *precisely the observed* first lines[57] recorded by Hulthén.[58]

For convenience of later reference, equations analogous to Eqs. (7) and (11) for the violet CN bands and to Eqs. (18) and (19) for the HCl and CuH bands are given here[59]; the equations for $\Delta_2 F'$ and $\Delta_2 F''$ would be exactly as in Eq. (17), so are not repeated:

$$\begin{gathered} R(j)=F'(j+1)-F''(j)\,; \\ Q(j)=F'(j)-F''(j)\,; \quad P(j)=F'(j-1)-F''(j) \end{gathered} \tag{18}$$

$$\begin{gathered} \Delta_1 F'(j)=R(j)-Q(j)=Q(j+1)-P(j+1) \\ \Delta_1 F''(j)=R(j)-Q(j+1)=Q(j)-P(j+1) \end{gathered} \tag{19}$$

---

[57] In Hulthén's notation these are $P(2)$, $Q(2)$ and $R(2)$.

[58] Except that in two out of four bands an additional R line is not recorded, having perhaps been overlooked on account of low intensity. Another interpretation of these bands accounting for the observed missing lines has been given by Kratzer[5], using integral j values and $\epsilon=\frac{1}{2}$. But this interpretation is decidedly forced, and is furthermore inapplicable to the closely related AlH bands (cf. II of this series).

[59] By analogy with the AlH bands which will be discussed in the following paper of this series, it is, however, probable that there are really two values of $F''(j)$ for each value of j'', so that there is really a latent doubling in the lines of the CO bands, but two small to be resolved experimentally, probably on account of the high stability of the molecule. If this is the case, Eqs. (19) and (20) are not strictly correct.

STATEMENT AND CRITICAL DISCUSSION OF THE POSTULATES AND THEIR IMPLICATIONS, AND SUMMARY OF RESULTS OF THEIR APPLICATION

Statement of postulates. With but slight generalization, the leading assumptions and conclusions of the preceding sections can be stated in the form of three postulates; these will be given in slightly different form than in an earlier paper.[1] In the postulates there is of course much that is not novel,—but of which full use is being made for the first time.

I. The electronic states of molecules can be characterized, in accord with Birge's recent postulate,[1,24] by a term-designation (such as ^1S or ^2P, in the notation of Russell and Saunders[32]) carrying implications similar to those for an atom; in particular, this is associated with an electronic quantum number j_e whose numerical value is identical (at least substantially) with *Sommerfeld's* atomic inner quantum number j for the given term-type; or in some cases each atom individually may possess a j_e, and in such cases the electronic states of the H atom are to be classed with those of an alkali metal.

II. The vector or vectors j_e set themselves parallel (ρ components) or perpendicular (σ components), or nearly so, to the vector m, and the rotational energy term is given in the general case substantially by a Kratzer-Kramers and Pauli formula (Eq. (8)).

III. The molecular j has integral values for odd molecules and half-integral values for even molecules, and is subject to the selection principle $\Delta j=0, \pm 1$, the relative intensities for these three transitions being governed by the correspondence principle.

Remarks on the evidence for the postulates. In the interpretation of any individual band spectrum, there are always various possibilities, the number of these depending on how much of a theoretical nature one assumes. For example, Kratzer's interpretation of the violet CN bands as here adopted, is by no means the only one for which considerable justification can be found.[11] Nevertheless, it gives an explanation of the observed structure, including the doublets, which is *at least* as simple and plausible as any that has been suggested. Similar statements are applicable to the interpretations of other band spectra given in the preceding section.

In most cases, the explanation given has, in the writer's opinion, the maximum of simplicity consistent with the observed degree of complexity of the experimental facts. E.g., in CuH and HCl, the interpretation adopted ($\epsilon'=\epsilon''=\sigma'=\sigma''=0$) is in effect that of the simple rotator (with half-integral rotational quantum numbers). In the case of CO, the necessity of departing a step from this simplest interpretation, in spite of the very simple arrangement of the branches, is definitely shown by the falling out of a line near the origin which is *present* in the cases of CuH and HCl. This new feature is accounted for by the new assumption $\sigma''=1$ instead of $\sigma''=0$. Again in the CH bands, it is difficult to see how a simpler interpretation of the observed relations could be devised.

In view of these facts, it must surely be significant that all these simple interpretations can be generalized into three plausible and simple postulates (so simple that their power is not at once evident); and that from these postulates all the above interpretations can be deduced at once, together with many more covering most of the band spectra whose empirical structure is sufficiently known. One of the great merits of the postulates is that they make very definite specifications, which render them freely open to experimental test. In this connection it is especially significant that no cases have yet been found which involve a certain contradiction of the postulates.

It should be stated that it appears to be impossible to obtain any consistent agreement with observation if any other systematic choice of j_e and j values is made than that embodied in the postulates as stated.

In spite of the above facts, it is very unlikely that the statement of the postulates given above represents anything final and complete. Formally and empirically, at least, it seems probable, however, that they represent a correct first approximation in ordinary cases at least.

Postulate I and the nature of molecular electronic states; *relation of magnetic susceptibilities to electronic states.* In spite of postulate I, important differences apparently exist between atomic and molecular electron states, as would indeed be expected. Thus molecular S states differ (cf. p. 491 and p. 500) from atomic S states in that their intercombination is not restricted, even in simple cases, by the azimuthal or inner quantum selection principles of line spectra. Likewise, P-P combinations occur.

Nevertheless, the similarity of any molecular electronic state to a corresponding atomic state may be supposed, until contradictions are found, to extend to such quantities as total quantum numbers, Landé g factors, and magnetic moments.

From this principle one may conclude, for all diamagnetic diatomic gases (H_2, CO, N_2, halogens, halogen halides, etc.) that $j_e=0$; a similar conclusion doubtless also applies to polyatomic gases. Further, at least in the case of gases whose molecules contain atoms of low atomic weight, we can interpret this as due to a ^1S normal state; for if the lowest excited state were of any other type, such as $^3P_0$, having $j_e=0$, an appreciable fraction of the molecules would be in paramagnetic slightly excited states, e.g., $^3P_1$ and $^3P_2$ in the case cited. This conclusion is supported by the band spectrum data in cases (CO, HCl) where data are available.

All odd molecules should, from the above principle, be paramagnetic, but such molecules are very rare in the gaseous state, on account of their chemical activity. The most familiar example is NO, whose normal state is apparently a mixture of paramagnetic $^2P_1$ and $^2P_2$ molecules (cf. Fig. 1). The paramagnetism of O_2 shows that its normal state cannot have $j_e=0$. The observed susceptibility is in very close agreement, according to calculations of Sommerfeld,[60] with that of an atom in an S state having $j_e=1$, i.e., a ^3S state. The fact that Curie's law is obeyed to low temperatures for oxygen[61] is strong evidence that only one type of O_2 molecule is present, not e.g., a mixture such as $^3P_0$, $^3P_1$, and $^3P_2$. The ultraviolet oxygen bands also give evidence, although not conclusive, in favor of a ^3S molecular state. But if the indicated correlation is correct, it involves the very surprising and hardly credible result that the O_2 molecule is oriented in a magnetic field in the same way as a ^3S atom, without regard to the rotational motion of the nuclei; for this assumption was involved in Sommerfeld's calculation.

Molecular and atomic j values. From the close analogy which has been shown to exist between molecular electronic states and corresponding atomic states, it seems altogether probable that the definite conclusions reached (and embodied in postulate *I*) as to j_e values in molecules apply directly to the j values of corresponding states of atoms.

Assuming this to be true, $j(=j_e)$ (cf. p. 487) is integral for even atoms and half integral for odd atoms, as supposed by Sommerfeld. But for molecules, according to postulate *III*, $j(\neq j_e)$ is half-integral for even diatomic molecules, and integral for odd diatomic molecules, as if Landé's J values were applicable here. This curious shift is illustrated by considering the process of adding a proton to a Cl^- ion. In the process, $j_e=j=0$ for the Cl^- ion is replaced by $j(\neq j_e)=\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$ for the molecule.

Other applications of the postulates. The results of the application of the postulates to known band spectra have an important bearing on the problems of molecular structure and molecule formation. The subject has been discussed briefly in previous papers,[2,38] and will be further discussed in connection with later papers.

The application of the postulates gives a new aid to decision in determining the emitter of a band spectrum.

---

[60] A. Sommerfeld, Atombau, 4th Ed. p. 637–41.

[61] Kammerlingh-Onnes and Perrier, Leiden Comm. 139d, p. 49, ref. 1.

The postulates necessitate a revised interpretation in cases where in the past quarter-integral quantum numbers have been assumed (He_2, cf. R. S. M., ref. 25; HgH, cf. ref. 2; etc.); essentially[62] only integers and half-integers are now used.[63]

Note added to proof.—According to the new quantum mechanics, the term Bj^2 in the expression for $F(j)$ should be replaced by $B(j+\frac{1}{2})^2$, or the latter plus a small constant. This has been shown in detail[64] only for the case $j_e=0$ (Eq. (8D) above), but presumably holds in general.[65] If so, and the new mechanics is correct, the true j values are all $\frac{1}{2}$ unit lower than was concluded above (the words "integral" and "half-integral" should then be interchanged in postulate *III*), and the "curious shift" just discussed under "molecular and atomic j values" disappears. Observed intensity relations (at least in bands of the HCl type) are also accounted for more simply than before. Kratzer's seemingly arbitrary exclusion of the state "$j=0$" (cf. p. 490) is now justified, and the absence of the null-line,[64,65] in the violet CN band-type is immediately accounted for by the fact that "$j=0$" would now become $j=-\frac{1}{2}$, which seems meaningless (or else necessarily identical with $j=+\frac{1}{2}$); the occurrence of "$j=0$" in the CH and OH bands (cf. p. 490) seems, however, to conflict with these results.

In a recent important paper,[65] Hund has discussed the interpretation of the phenomena of electronic multiplicity and of fine structure in band spectra. Hund's theoretical deductions have a close relation to the more empirical results of the present series of papers. The subject will probably be further treated later.

In conclusion, the writer wishes to express his appreciation of the valuable suggestions and criticism of Professor E. C. Kemble and Professor R. T. Birge.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
June 15, 1926

---

[62] This qualification is to take account of the usual small deviations of j_e from an exact integer or half-integer.[1]

[63] The only apparent outstanding exception is CaH band described by the writer (Phys. Rev. **25**, 509 (1925).

[64] L. Mensing, Zeits. f. Physik **36**, 814 (1926); I. Tamm, Zeits. f. Physik **37**, 685 (1926); E. Fues, Ann. der Physik **12**, 367 (1926).

[65] F. Hund, Zeits. f. Physik **36**, 657 (1926).