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²⁰ W. Pauli, Jr., *Zeit. Physik.*, **31**, 765, etc. (1925).
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SYSTEMATIC RELATIONS BETWEEN ELECTRONIC STRUCTURE AND BAND-SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. II. THE ZnH, CdH AND HgH MOLECULES AND THEIR SPECTRA

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Communicated February 15, 1926

Introduction.—In a previous paper,¹ which will here be referred to as *I*, certain postulates were set up for the interpretation and prediction of the structure of band spectra. These will be applied in the present paper to the very instructive spectra of ZnH, CdH and HgH and in subsequent papers to the spectra of other molecules.

In the analysis of band spectra, the application of the Ritz combination principle does not yield directly the rotational energy function $F(j)$ —cf. *I*—for the molecule, but only *differences* of this function, of the forms $\Delta_2 F(j) = F(j+1) - F(j-1)$, from *P,R* combinations, and $\Delta_1 F(j) = F(j+1) - F(j)$, from *P,Q,R* combinations. The general expressions for these, corresponding to the expanded form (Eq. 1A) of equation 1 of *I* are:

$$(2A) \Delta_1 F(j) = 2B(j + \frac{1}{2} \mp \epsilon) \mp B\epsilon\sigma^2/j(j+1) + \dots$$

$$(3A) \Delta_2 F(j) = 4B(j \mp \epsilon) \mp 2B\epsilon\sigma^2/(j^2 - 1) + \dots$$

From equations (2A) and (3A) it will be seen that the simultaneous presence of ϵ and σ can be determined experimentally from ΔF only when both ϵ and σ^2 are reasonably large. If *either* ϵ or σ is *alone* present (or if either is so small that $\epsilon\sigma^2$ is too small to detect), equations (2A) and (3A) assume the empirical forms $\Delta_1 F = 2B(T + \frac{1}{2} \pm \gamma)$ and $\Delta_2 F = 4B(T \pm \gamma)$. Here $\gamma < < \frac{1}{2}$, and T , which will be called the effective rotational quantum number, has in practice nearly integral values (τ), or half-integral values (τ^*). From ΔF alone it is thus impossible to distinguish between the cases (1) σ appreciable, ϵ absent (or very small); (2) σ absent (or very

small), ϵ appreciable; (3) both ϵ and σ small or absent; the indistinguishability of cases (1) and (2) was first pointed out to the writer by Prof. E. C. Kemble. E.g., half-integral T values may arise *either* from half-integral j values, with $\epsilon = 0$, and σ present or absent, *or*, from integral j values with $\epsilon = \pm \frac{1}{2}$, and σ absent; integral T values (such as occur in the initial states of the HgH type bands) are comparatively rare in known bands, but their occasional occurrence is very significant. Escape from these ambiguities is afforded by the postulates, especially 3, of *I*, and the correctness of the results is attested by their complete consistency in all cases so far investigated.

It will frequently be necessary in the following to distinguish between terms for which ϵ is positive (parallel to m) and those in which it is negative (anti-parallel position). The former will be given the subscript 1, the latter, the subscript 2; thus $F_1(j) = B(j-\epsilon)^2 + \dots$, while $F_2(j) = B(j+\epsilon)^2 + \dots$. This nomenclature will also be extended to certain cases where there is a double rotational term of the σ type, with $\epsilon = 0$, or nearly so, or having two numerically different values of ϵ ; in such cases the choice of designation is determined by analogy in behavior to the more usual cases.

Distinction between a more and a less excited state will be made by attaching superscripts—thus F' , B' , ϵ' , etc., will refer to the *more excited* electronic state, F'' , B'' , ϵ'' to the *less excited* state.

In general, six branches are then to be expected for any band, as follows (cf. *I*, supplementary remark 5): $P_1(j) = F'_1(j-1) - F''_1(j)$; $P_2(j) = F'_2(j-1) - F''_2(j)$; $Q_1(j) = F'_2(j) - F''_1(j)$; $Q_2(j) = F'_1(j) - F''_2(j)$; $R_1(j) = F'_1(j+1) - F''_1(j)$; $R_2(j) = F'_2(j+1) - F''_2(j)$. It will be seen that P , Q and R branches are here implicitly defined as branches for which Δj has the respective values $+1$, 0 and -1 . The *appearance* of any branch is determined by the values of B and Δm , and from this standpoint, a considerable variety of band-types is to be expected—and is observed. Also there are types in which various branches are missing, or in which certain branches are coalescent.

As stated in *I*, the Russell-Saunders notation will be used in designating electronic states.

Interpretation of ZnH, CdH, HgH Bands.—The spectra of these molecules have been studied in recent years especially by Hulthén^{2,3} and by

TABLE I
DOUBLET AND TRIPLET SEPARATIONS FOR 2 P TERMS

	MeH	M(² P _{1,2})	Me(³ P _{1,2})	Me(³ P _{0,1})	Me ⁺ (² P _{1,2})
Zn	330	248 (Cu)	389	190	874 (?)
Cd	1001	921 (Ag)	1171	542	2482
Hg	3683	3815 (Au)	4630	1767	9829 (??)

Kratzer.^{4,5} The evidence that the emitters are those named seems conclusive.^{4,6,7} For each molecule, there are two closely related band systems having a common final state. Hulthén has shown an important

parallelism between these two systems and the transitions $2\ ^3P_{1,2} - 1\ ^1S$ of the respective metal atoms.⁸ The writer, however, believes that the correct formulation is $2\ ^2P_{1,2} - 2\ ^2S$. The observed separations $P_1 - P_2$ are compared in table 1 with the doublet separations of the comparable atoms Cu, Ag, Au, with the triplet separations of Zn, Cd and Hg, and with the doublet separations of Zn^+ , Cd^+ and Hg^+ .

The recorded observations on intensity^{2,9} indicate that the low-frequency systems of ZnH, CdH, HgH are more intense than the high-frequency systems, and so suggest that the $2P$ doublet is inverted. But this is conclusively disproved by the evidence from the missing lines (see below). One might, then, conclude that the intensity rules of line spectra are inapplicable here, but such a conclusion is hardly justified as yet.⁹

Table 2 shows that the molecular stability, as gauged by the vibration frequency ω_0 and the nuclear separation r_0 , is markedly greater for the more excited states of the molecule; this relation was first pointed out by Hulthén,^{3,8} also by Ludloff.⁵ The correlation of r_0 with the ionization potential of the metal is no doubt due to the fact that the latter should vary qualitatively inversely as the atomic or ionic radius; thus the equilibrium distance between the nuclei of the two atoms is evidently largely dependent on the radius of the metal atom or ion. A completely parallel variation of r_0 with the ionization potential of the atom occurs in the series CuH, AgH, AuH. The comparatively large values of r_0 show, as pointed out by Kratzer,⁴ that the union of the H and metal atoms is here quite different in character from that in HCl, HBr and the like, where the H^+ ion loses its electron and penetrates the outer shell of the negative ion.

TABLE 2
MOLECULAR CONSTANTS FOR ZNH, CDH AND HGH*

		B'	$r_0'(A. U.)$	ω_0'	T'	B''	r_0''	ω_0''	T''	ION. POT. OF Me
ZnH	P_1	7.15	1.54		$\tau \pm 0.01$	6.54	1.60	1552	$\tau^* \pm 0.01$	9.35 v.
	P_2	7.47	1.50		$\tau \pm 0.00$					
CdH	P_1	5.96	1.67		$\tau \pm 0.02$	5.33	1.76	1374	$\tau^* \pm 0.03$	8.95 v.
	P_2	6.03	1.66		$\tau \pm 0.00$					
HgH	P_1	6.56	1.60	(1995)	$\tau \pm 0.13$	5.38	1.74	1308	$\tau^* \pm 0.095$	10.39 v.
	P_2	6.61	1.58	(2180)	$\tau \pm 0.00$					

* The data are taken from, or based on, the papers of Hulthén, Kratzer and Ludloff. The ω_0'' values, and the ϵ values for HgH, are revised values kindly supplied by Prof. R. T. Birge. The ω_0' values are calculated from a theoretical relation between ω_0 , B and the coefficient of j^2 .

In both band systems, for each emitter, each band has six branches, for which $\Delta T = -1\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -1\frac{1}{2}, +\frac{1}{2}, +1\frac{1}{2}$, and which are due to combinations of the two τ -type initial and two τ^* -type final terms; these branches are interpreted by Kratzer⁴ as $R_1, R_2, Q_1, Q_2, P_1, P_2$, respectively. For the representation of these bands Kratzer has assumed equations of the form (cf. I) of equation (1C) for both states, but with an

added linear term $\pm 2\delta j$. His values of δ are small, and he concludes $\epsilon' = 0$, $\epsilon'' = \frac{1}{2}$, for ZnH and CdH^{4,10} and for the high-frequency system of HgH⁵; but for the low-frequency system of HgH, his δ values are large, and he concludes $\epsilon' = \frac{1}{2}$, $\epsilon'' = \frac{1}{4}$. It seems to the writer that the close analogy shown in table 2 between the spectra of the three molecules is nearly conclusive evidence against this special interpretation of Kratzer's for one system of HgH bands, in spite of Kratzer's very strong evidence in its favor; this evidence consists (ref. 4, p. 93) in certain numerical relations which must now apparently be regarded as fortuitous, although the matter deserves further investigation. Furthermore, the theoretical justification of Kratzer's linear term has been called in question by Birge and Kemble.¹¹ The observed ΔF values can be expressed without the use of a linear term, by using ϵ values which depart somewhat from exact integers or half-integers (and which may increase¹² with j). Table 2 then shows a very systematic variation with atomic weight in the departures of ϵ from 0 or $\frac{1}{2}$.

A formally comparatively slight change in Kratzer's interpretation (as already modified above by the suppression of the linear term) of the HgH type bands serves to make them fit the postulates of *I*. Integral values of j , required for odd molecules by postulate 3, have already been assumed by Kratzer. From table 2, ϵ'' has in all cases approximately the value $\frac{1}{2}$. Also, $\sigma'' = 0$, or nearly so, for otherwise an $\epsilon\sigma^2$ term in $\Delta F''$ would have made itself evident. For both initial states, $\epsilon' = 0$, approximately, but, as shown in the introduction, we cannot determine from the $\Delta F'$ values whether or not a σ is present. But the presence of *Q* branches—their intensity is about the same as that of the *P* or *R* branches—gives evidence (although not in itself conclusive—cf. *I*, paragraph 5), in favor of the presence of a σ due to the emitting electron. In view of the evidence that the two initial electronic terms are 2P_1 , and 2P_2 , the assumptions $j'_e = \frac{1}{2} = \sigma'$ (approximately) for the low-frequency systems, and $j'_e = \frac{3}{2} = \sigma'$ (very nearly) for the high-frequency systems, seem justified. The assignment of $j'_e = \frac{1}{2}$ to the apparently more intense system is based upon the evidence of the "missing lines."

The deviations of ϵ' from 0 and of ϵ'' from $\frac{1}{2}$ are largest in the HgH bands. If $j'_e = \frac{1}{2}$ or $\frac{3}{2}$ exactly, the deviations must mean that σ' falls below $\frac{1}{2}$ or $\frac{3}{2}$, and similarly, if $j''_e = \frac{1}{2}$ exactly, that $\sigma'' \neq 0$. Then from j_e and ϵ we can in each case calculate σ , since $j_e^2 = \epsilon^2 + \sigma^2$. The following equations result (for higher power terms, cf. refs. 4, 5); in each case the upper sign of ϵ belongs to F_1 , the lower to F_2 :

$$(4) \quad \begin{cases} F'_{1,2}(P_2) = 6.61(\sqrt{j^2 - (1.500)^2} \mp 0.00)^2 + \dots\dots\dots \\ F'_{1,2}(P_1) = 6.56(\sqrt{j^2 - (0.483)^2} \mp 0.13)^2 + \dots\dots\dots \\ F''_{1,2}(S) = 5.38(\sqrt{j^2 - (0.294)^2} \mp 0.405)^2 + \dots\dots\dots \end{cases}$$

Here σ'' is surprisingly large; nevertheless it will be seen by a consideration of numerical magnitudes in equation (2A) that the effect of the $\epsilon\sigma^2$ term in $\Delta F'(P_1)$ and in $\Delta F''$ will be detectable only by very accurate measurements on the lines of lowest j ; the data now available seem inadequate for a decision. In the cases of CdH and ZnH, the calculated σ'' values are very small.

The "missing lines" of a band are determined—in a way originally pointed out by Lenz—by the fact¹³ that, in equation (1) of I , j cannot be less than σ . This rule determines, for each of the six terms of equation 4, a minimum value of j , which may be denoted j_{\min} . These values are 2 for $F'_{1,2}(P_2)$, 1 for $F'_{1,2}(P_1)$ and 1 for $F''_{1,2}$. In any particular branch of a band, the smallest possible pair of j values (j' , j'') is determined, in a fairly obvious manner, sometimes by j'_{\min} , sometimes by j''_{\min} .

For the transition ($P_1 \rightarrow S$) here, the predicted first lines for the various branches are, in terms of initial and final j values ($j' \rightarrow j''$): $P_{1,2}$, (1 \rightarrow 2); $Q_{1,2}$, (1 \rightarrow 1); $R_{1,2}$, (2 \rightarrow 1). The observed first lines as recorded by Hulthén^{2,3} are (a * means that the observed line is superposed on another line, so that the result is not wholly conclusive): ZnH λ 4326, $P_1(1 \rightarrow 2)$; $P_2(1 \rightarrow 2)$; $Q_1(1 \rightarrow 1)^*$; $Q_2(1 \rightarrow 1)$; $R_1(2 \rightarrow 1)^*$; $R_2(2 \rightarrow 1)$, but the calculated position of $R_2(1 \rightarrow 0)$ is practically the same as for $Q_2(1 \rightarrow 1)$, so that the result is inconclusive for R_2 ; CdH λ 4510, $P_1(1 \rightarrow 2)$; $P_2(3 \rightarrow 4)$; $Q_1(1 \rightarrow 1)$; $Q_2(3 \rightarrow 3)$; $R_1(3 \rightarrow 2)$; $R_2(3 \rightarrow 2)$, but here and in HgH λ 3728 the data are doubtless incomplete; in HgH $\lambda\lambda$ 4017 and 4219, where the data are most reliable, the agreement with prediction is complete. The agreements above noted are extremely satisfactory, in view of the experimental uncertainties. However, the absence of lines for which j' or $j'' < 1$ cannot be considered quite conclusively proved without further very careful study; nevertheless, there appears to be no definite evidence in Hulthén's data for the presence of any such lines.

In its prediction of missing lines for the bands above considered, the present interpretation differs from Kratzer's only in one respect. The absence of lines for which j' or j'' is zero is here attributed to the presence of an appreciable σ , whereas Kratzer was forced to make the arbitrary assumption that $j = 0$ is excluded. In a later discussion of the CH bands, however, it will be shown that this arbitrary exclusion is definitely not justified, since at least one line is unquestionably present for which $j' = 0$, σ also being zero. Hence the observed absence of $j' = 0$ and $j'' = 0$ in the present case is strong evidence in favor of the assumed existence of a σ' and a σ'' .

For the transition ($P_2 \rightarrow S$), the predicted first lines are: $P_{1,2}(2 \rightarrow 3)$; $Q_{1,2}(2 \rightarrow 2)$; $R_{1,2}(2 \rightarrow 1)$. These are precisely the observed first lines in ZnH λ 4260 [Hulthén gives also $P_1(1 \rightarrow 2)$ and

$P_2(1 \rightarrow 2)$, but both are*], in CdH λ 4300 [except that Hulthén reports $P_1(1 \rightarrow 2)$, but the recorded line is exceedingly weak and slightly displaced] and in HgH λ 3500.^{2,3} Since the missing lines in these bands have not hitherto been explained and could not be explained by Kratzer's interpretation, the correctness of the present interpretation for both systems of bands seems very strongly supported by this evidence.

The low stability of the HgH molecule in the 2S state is shown especially by Hulthén's work,³ in which he finds from the spectrum a heat of dissociation corresponding to only 0.37 volt. Although the impossibility of determining directly the existence of a small σ'' makes impossible a *direct* exact evaluation of j_e'' ($j_e'' = \sqrt{\epsilon''^2 + \sigma''^2}$), our assumption $j_e'' = \frac{1}{2}$ (or nearly so) is obviously strongly supported by the observed ϵ'' values, and by the testimony of the missing lines, for HgH, CdH and ZnH. The molecule in its less excited state may then in each case be pictured as composed of a neutral, relatively inert, metal atom in its normal 1S state ($j_e = 0$), to which the H atom ($j_e = \frac{1}{2}$) is loosely attached by secondary (van der Waals) forces, converting the 1S state of the atom into a 2S molecular state (cf. conclusions 1 and 3 in *I*). The orbit of the H electron is then approximately of the ϵ -type, $\epsilon = \pm \frac{1}{2}$ corresponding to a rotation of the electron in the same or opposite sense, respectively, to that of the nuclei.

The greatly increased stability of the molecules in their P states can be explained as follows: *one* of the metal valence electrons becomes excited and passes into an essentially σ -type 2_2 orbit, while the remaining n_1 electron becomes coupled with the 1_1 H electron so that $j_e = 0$ (or nearly so) for this pair of electrons. The nature of this coupling is doubtless the same as that which occurs in CuH, AgH, AuH and probably AlH, and will be discussed later in connection with the spectra of these molecules. The 2_2 electron is now in the same condition as in a doublet atom, hence there are two terms 2P_1 and 2P_2 . The fact that the doublet separations in ZnH, CdH and HgH, respectively, agree well with those of neutral Cu, Ag or Au atoms (table 2), shows that the two electrons in n_1 orbits exert a considerable screening effect.

The considerable difference in r_0 (table 2) for the P_1 and P_2 states indicates a real difference in shape or position of the electron orbits in the two cases; and the marked difference in the ϵ values is also undoubtedly significant.

For the P_2 states, the existence of a double (perhaps even quadruple) rotational term F'_1, F'_2 , in spite of the absence of an appreciable separation of a $\pm \epsilon$ or any other type between the term values, is shown unquestionably by certain perturbations.^{3,5} The vanishing of ϵ probably shows that the electron orbit—which would here be expected to be truly circular—lies in a plane exactly perpendicular to the figure-axis.

The non-vanishing of ϵ in the case of the P_1 orbit indicates that the latter is *inclined* with respect to the internuclear axis. It seems possible that this is due to a tendency of the solitary P electron to become coupled with the other metal electron. Similarly, the presence of a σ in the final state might be due to a tendency of the isolated H electron to become coupled with one of the metal electrons, thus forcing the other into a different plane.

The assumption that j_e can divide itself between ϵ and σ has been shown, in the case of the transition $P_1 \rightarrow S$, to afford a simple explanation (1) of the occurrence of deviations of ϵ from 0 or $\frac{1}{2}$ in connection with the phenomenon of rotational doubling, and (2) of the otherwise inexplicable absence of the state $j'' = 0$. But the persistence of rotational doubling for orbits of the σ -type, even when ϵ vanishes (P_2 states here; spectrum of AlH, etc.), shows pretty definitely that this doubling must arise from a deeper cause, of which the above deviations are but one manifestation. The writer hopes to discuss the problem more fully in a later paper. Whatever may be the ultimate explanation of rotational doubling, it is, however, evidently very important to make conclusive the already very strong evidence that j_e can be divided between ϵ and σ (the simultaneous presence of ϵ and σ in the final state of the CH bands is probably due to the *separate* j_e values of the two atoms). New very accurate measurements on the lines of small j in the HgH bands, and conclusive proof of the absence, in the bands of the low-frequency system, of the lines $R_2 (1 \rightarrow 0)$ and $R_1 (1 \rightarrow 0)$, should settle this question. But, as will be shown in later papers, it is probable that in *most* band spectra the apparent deviations of ϵ from 0 and $\frac{1}{2}$ cannot be accounted for as here by the presence of a σ , but are probably due to some as yet unknown cause, so that something like Kratzer's linear term may after all be applicable.

Since, according to the postulates of I , the structure of a band system depends only on the type of electronic transitions involved, we may expect for the transition ${}^2P_{1,2} \rightarrow {}^2S$ in *all* molecules a structure essentially the same as in the HgH bands; and for ${}^2S \rightarrow {}^2P_{1,2}$ a structure differing only in respect to the missing lines—assuming, however, in both cases that the S orbit is of the ϵ type and that the P orbits are of the σ type. As will be shown in a later paper, these expectations are confirmed, so far as can be seen from the available data, in the cases of the BO, CN, CO⁺, NO and alkaline earth halide bands.

¹ R. S. Mulliken, these PROCEEDINGS, March, 1926.

² E. Hulthén, Dissertation, Lund, 1923, "Über die Kombinationsbeziehungen unter den Bandenspektra."

³ E. Hulthén, *Zeit. Physik*, **32**, 32 (1925)—HgH bands.

⁴ A. Kratzer, *Ann. Physik.*, **71**, 89 (1923).

⁵ H. Ludloff, *Zeit. Physik*, **34**, 485 (1925).

⁶ R. S. Mulliken, *Nature*, **13**, 489 (1924).

⁷ K. T. Compton and L. A. Turner, *Phil. Mag.*, **48**, 360 (1924); *Physic. Rev.*, **25**, 606 (1925); Compton, McCurdy and Turner, *Physic. Rev.*, **24**, 608 (1924); etc.

⁸ E. Hulthén, *Nature*, Oct. 31, 1925.

⁹ Dr. Hulthén has been so kind as to inform the writer that the high-frequency system is *much* weaker than the low-frequency system in HgH, *decidedly* weaker in CdH and about *equally intense* in ZnH. It seems likely that the conditions of excitation play a dominant rôle, masking the effect of the difference in a priori probabilities of the two excited states. Howson's CdH photographs (*Astrophys. J.*, **36**, 291, 1912) agree with Hulthén's statement.

¹⁰ This includes an alteration of his published values⁴ of δ' and ϵ' for ZnH (private communication).

¹¹ Cf. E. C. Kemble, *J. Opt. Soc. Amer.*, **12**, 1 (1926): footnote on p. 4.

¹² R. T. Birge, *Physic. Rev.*, **27**, probably Feb., 1926 (Abstracts).

¹³ W. Lenz, *Verh. d. D. Phys. Ges.*, **31**, 632 (1919); H. A. Kramers and W. Pauli, *Zeit. Physik*, **13**, 351 (1923).

THE ELECTRONIC STATES OF THE HELIUM MOLECULE

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Communicated February 5, 1926

Extending tentative suggestions of the writer,¹ Birge has recently² made an important step in putting forward the hypothesis, which he supports by much valuable evidence, that the electronic states in molecules are essentially similar to those in atoms—so that, in particular, the molecular states may appropriately be designated by term symbols (¹S, ²P, etc.), corresponding to those used (notation of Russell and Saunders) in line spectra. In applying this hypothesis to the structure of various band spectra, the writer has found that it leads successfully to many interesting results which will be discussed in separate papers. In the course of this work, a study of the structure of the helium bands gave definite evidence in favor of the designation $2S-mP$ ($m = 3, 4, 5, \dots$), the terms being of a singlet type, for the "main" series of helium bands, which have been found to obey a line series law^{3,4}; and in favor of an identical designation in the case of the "second" series of bands. This evidence will be given in a later complementary paper.

It seems possible that the relatively intense "main" series is emitted by a molecule composed in its least excited state of two helium atoms in metastable $2S$ "doublet" states, and the weaker "second" series by a molecule composed of two metastable $2S$ singlet atoms; the evidence is given in the last paragraph. The relative intensity of the two systems is then qualitatively what might have been expected on the basis of stability