Zeeman Effect in Diatomic Molecular Spectra

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§1. INTRODUCTION

THE history of the study of the effect of magnetic fields on the spectra emitted by molecules (and for practical reasons only diatomic molecules need be considered) presents a striking example on the one hand of the slow progress made when no objective theory is present to guide experimental work—and on the other, of the rapidity of progress once such guidance is available.

The earlier workers[1] naturally selected for examination principally molecules whose spectra could be excited with high intensity. Again since the effects which the magnetic field produced were rather smaller and less striking than those found in atomic spectra, in most cases fields of such high intensity were employed as to obscure many of the more important features. Furthermore, unhappily, the bands chosen were without exception either those giving only minor second order effects or of the more complicated types involving many closely packed branches in each band. As a result the dispersion and resolving power of the instruments used were hardly sufficient for a characterization of the diversity of patterns obtained. Later work has in fact shown that even with the largest gratings at present available only a small fraction of the Zeeman patterns to be expected can ever be clearly resolved—the remainder at best affording only semiquantitative information.

Progress in the investigation and interpretation of Zeeman-effects in diatomic spectra, as is

[1] For an excellent brief review of work up to its time of publication see Jevon's *Report on the Spectra of Diatomic Molecules*. For notation used here see either Jevon's Report or Mulliken's *On the Interpretation of Band Spectra*, Parts I, IIa, IIb, Rev. Mod. Phys. **2**, 60 (1930); Part IIe, ibid. **3**, 89 (1931); Part III, ibid. **4**, 1 (1932). These latter will simply be referred to as Mulliken's Review I, etc.

only natural, has been closely connected and in fact limited by the current state of knowledge of the constitution and nature of the spectra themselves. The work therefore falls rather definitely into three periods.

During the first, from say 1908 to around 1913, the origin and structure of the bands studied were imperfectly known and numerical relations within a band were, where possible, expressed in Deslandres' series, counting the individual band lines from the head of the band. This tended to disguise many important similarities in the behavior in the field of individual branches (or series) and the rather fragmentary observations which were recorded were often the least significant from the standpoint of later theory.

The second period from about 1914 to 1923 was characterized by the use of higher dispersion apparatus, the recognition by Fortrat[2] of the importance of numbering branches from the band origins rather than the band heads, and the general interpretation of diatomic spectra in terms of the conventional quantum theory. The Zeeman-effect data in turn were more complete and detailed and capable therefore of more adequate comparison with later findings.

The empirical results obtained in the first two periods will be referred to later in terms of the detailed theory but may be summarized in part briefly as follows:[3]

1. The Zeeman patterns of band lines are often of the size of those in atomic spectra but usually smaller and apparently incompletely resolved.

2. The earlier lines in a branch are the most sensitive, different branches in the same band often differing markedly in their behavior.

3. The Zeeman patterns are usually more or less unsymmetrical around the no field position and exhibit polarizations which are either *similar* or *reversed* when compared with the patterns of well-known atomic lines such as the D-lines of sodium.

4. As higher fields are used the narrow doublet and triplet members of multiplet branches are drawn together with a consequent apparent simplification in the overall appearance of the band.

The third period from 1923 to the present time, began with the appearance of a brief discussion by Kramers and Pauli[4] of the energy-splitting of molecular terms in a magnetic field to be expected on the basis of the older quantum theory. This discussion unfortunately was appended to a rather long account of another subject and failed to attract the attention which it deserved. In 1926 Kemble[5] independently gave a more detailed discussion and inaugurated the experimental test of his predictions in the Angstrom bands of CO. In the same year Hund[6] considered briefly the effect of the field on molecules representing his case (a) and case (b) types of molecular coupling. At almost the same time Van Vleck[7] obtained for a rigid molecule the results to be expected on the new quantum mechanics and discussed their application to the hydrogen molecular spectrum. The significance of these and the later discussions of more complicated systems in terms of quantum mechanics can best be appreciated after an examination of the fundamental similarities and differences exhibited by *atomic* and *molecular* systems in the magnetic field.

§2. Zeeman Splitting of Atomic and Molecular Energy Levels

As has been pointed out many times before, the magnetic separation of energy levels in the case of molecules owes its existence to the same fundamental causes as in atoms. In each case we have a mechanical gyroscope (assumed rigid for the moment) possessing a *magnetic moment.* The external magnetic field due to this moment exerts a torque, which in the case of a bar magnet would simply cause orientation along the field, but which due to the gyroscopic forces in the atomic or molecular case causes steady precession around the direction of the field with the well-known Larmor frequency. If the magnetic moment in a given case is zero then of course the system remains insensitive to the field. In any event the magnetic energy is equal to the negative of the scalar product of the field $\mathbf{H}$ and the (average if it is not constant) magnetic

[2] Fortrat, Ann. de Physique **3**, 282 (1915).

[3] For more detailed discussion of the earlier work see in particular reference 4, Weizel *Banden Spektren* and Jevon's excellent summary in his *Report on Band Spectra of Diatomic Molecules.*

[4] Kramers and Pauli, Zeits. f. Physik **13**, 351 (1923).

[5] Kemble, Phys. Rev. **27**, 799 (1926); Bull. Nat. Res. Council **57**, 331–56 (1926).

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

[7] Van Vleck, Phys. Rev. **28**, 1006 (1926). See also Kronig, Zeits. f. Physik **46**, 814 (1927).

moment vector, $\mathfrak{y}$, of the system. Thus if E is the (average) magnetic energy,[7a]

$$E=-(\overline{\mathfrak{y}\cdot\mathbf{H}}). \tag{1}$$

Furthermore the total mechanical angular momentum of such a system is a quantized vector and therefore may take on only values which are multiples of $h/2\pi$. If we measure this mechanical momentum in units of $h/2\pi$ then it can be represented by a vector $\mathbf{J}^*$ where $|\mathbf{J}^*|=[J(J+1)]^{\frac{1}{2}}$ and J may assume only integral (or half integral) values. Then from the principle of space quantization only those orientations of $\mathbf{J}^*$ with respect to $\mathbf{H}$ are permissible for which the projection of $\mathbf{J}^*$ on $\mathbf{H}$ assumes integral (or half integral) values. If we call these M, M is the magnetic quantum number and can assume the $2J+1$ values $M=J$, $J-1\cdots-(J-1)$, $-J$. Hence each energy state is broken up by the field into $(2J+1)$ sub-states and therefore the average magnetic energy, E, is

$$E=-\overline{\mu\cos(\mathfrak{y},\mathbf{H})}H.$$

If now $\mathfrak{y}$ is not along $\mathbf{J}^*$ it will in general (with no field) move around as the system rotates and therefore have some average magnitude $\bar{\mu}$ over a cycle along the constant direction of $\mathbf{J}^*$. In the field, if the Larmor frequency of precession is small compared with the frequency associated with $\mathfrak{y}$ (which it is for small enough fields) we then have

$$E=-\bar{\mu}\cos(\mathbf{J}^*,\mathbf{H})H, \tag{2}$$

where

$$\cos(\mathbf{J}^*,\mathbf{H})=M/|\mathbf{J}^*|$$

and therefore

$$E=-M(\bar{\mu}/|\mathbf{J}^*|)H, \qquad M=-J,\cdots+J \tag{3}$$

or

$$E=-M\left[\frac{\text{average magnetic moment along } \mathbf{J}^*}{\text{total angular momentum of system}}\right]\cdot H. \tag{4}$$

If we measure $\bar{\mu}$ in units of the Bohr magneton, $eh/4\pi m_0c$ ($=0.918\times10^{-20}$ erg gauss^{-1}), and call[7a] $\bar{\mu}=-meh/4\pi m_0c$ we have

$$E=M(m/\mathbf{J}^*)(eh/4\pi m_0)H,$$

or dividing by hc to express energy in frequency units and writing $\Delta\nu_n$, the *half width* of the normal Zeeman atomic triplet, for $eH/4\pi m_0c$ [8]

$$W=E/hc=M(m/|\mathbf{J}^*|)\Delta\nu_n=-M\times\left[\frac{\text{average magnetic moment in Bohr magnetons along } \mathbf{J}^*}{\text{total mechanical angular momentum in Bohr units}}\right]\times\Delta\nu_n. \tag{5}$$

In the case of atoms the ratio in the brackets is simply the Landé splitting factor g and the size of the denominator is determined by the mechanical properties of electrons—and in the units employed—is always of the same general order of magnitude as the numerator. For singlet atomic states, where the electron-spin $\mathbf{S}^*$ is zero, its value is unity. When $\mathbf{S}^*\neq0$ and the field is so small as not to uncouple $\mathbf{S}^*$ and the orbital angular momentum $\mathbf{L}^*$, we have $\mathbf{S}^*$ and $\mathbf{L}^*$ precessing around their resultant $\mathbf{J}^*$. The components of $\mathfrak{y}$ $\perp$ to $\mathbf{J}^*$ cancel over a cycle and the projection on $\mathbf{J}^*$ is the average value, $\bar{\mu}$ referred to in the ratio g, where

$$g=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{6}$$

In the case of a molecular system we can continue to refer to the ratio in the brackets (in Eq. (5)) as the g-factor. Here, however, although $\mathfrak{y}$ may have values of the same order as those found in atoms, $\bar{\mu}$ is the average projection of $\mathfrak{y}$ on $\mathbf{J}^*$, which may be small when $\mathfrak{y}$ and $\mathbf{J}^*$ are nearly $\perp$, while $\mathbf{J}^*$,—except for the lowest rotational states,—is determined by the rotation of the heavy nuclei. Hence the value of g and therefore the spacing of the magnetic-sublevels may become very small for large values of J. On the other hand, the *number* of the sublevels goes up as $(2J+1)$ just as before. Hence even in the simplest molecular case we

[7a] It must be remembered that because of the negative electronic charge, the constant of proportionality between magnetic moment and angular momentum is *negative*. In this paper we use e as the numerical magnitude of the electronic charge. This gives the same result as if we considered the magnetic moment and angular momentum vectors as *parallel*, rather than anti-parallel, and used a + instead of a − sign in Eq. (1).

[8] Here $\Delta\nu_n=4.67\times10^{-5}H$ cm^{-1} when H is in gauss. Hereafter to avoid the frequent repetition of "half-normal Zeeman triplet width," $\Delta\nu_n$ will be referred to as one "Zeeman unit" where of course the absolute size of the unit is a function of the field strength H.

are confronted with a multiplicity of levels and a smallness of scale having no direct counterpart in atomic spectra.

The Zeeman *patterns* in a given band line are now to be predicted from the transitions between the sublevels of the two states involved with the same selection rules obtaining for changes in M as in atomic spectra, *viz.*, $\Delta M=0$ or ± 1. For observation at right angles to the magnetic field $\Delta M=0$ corresponds to light polarized $\parallel$ to **H** and $\Delta M=\pm 1$ to that polarized $\perp$ to **H**.

The characteristic behavior of a given molecular term is determined only when μ is averaged properly along **J***, and the value of μ depends not only on the sizes of **L*** and **S*** and on their relative orientation but on other factors. In particular it depends on their relative coupling energies with one another and with the rest of the molecule and with the way this coupling is affected by (1) the rotation of the molecule itself which sets up a magnetic field along the axis of rotation and (2) the external applied field. It is convenient to refer in general terms to the coupling energy between say **S*** and **L*** as $I(\mathbf{S}^*, \mathbf{L}^*)$ or between **L*** and the internuclear axis as $I(\mathbf{L}^*, \mathbf{ax})$, etc. Only in certain cases of course do we know the actual form of these functions but their general relative magnitudes enable the important physical cases to be classified under the Hund-types of coupling. To avoid the necessity of repeated reference to other sources these will be briefly characterized here.[9]

§3. Hund's Coupling Types in Diatomic Molecules

The electrons in a molecule at rest move in an electric field which is symmetrical about the nuclear axis and the interaction of **L*** and this axial field, $I(\mathbf{L}^*, \mathbf{ax})$ causes **L*** to precess around the direction of this field and the resultant average magnetic moment along this axis interacts in turn with the electron spin **S***. When rotation of the nuclei sets in, a magnetic field more or less pronounced is set up along the axis of the rotation. If **O** be a vector along this axis measuring the total angular momentum of the system $\perp$ to the axis of figure then $I(\mathbf{L}^*, \mathbf{O})$ and $I(\mathbf{S}^*, \mathbf{O})$ determine how the molecule is distorted as rotation increases. Here of course if **O** includes no magnetic moment those interactions vanish.

Hund's case (a)

Here $I(\mathbf{L}^*, \mathbf{ax})$ is very large compared with any other interactions involved and is essentially of an electric nature. **L*** precesses rapidly about the nuclear axis and gives a quantized projection, Λ, along the axis, where $\Lambda=0, 1, 2 \cdots$. The magnetic moment associated with Λ then has a *magnetic* coupling energy $I(\Lambda, \mathbf{S}^*)$ with **S*** which causes the latter to precess around the same axis giving a quantized projection Σ which may take on integral (or half integral) values. Hence **L*** and **S*** each precess in a similar fashion but for different reasons. Λ and Σ then add to **O** to give the total angular momentum, **J***, of the molecule, where $|\mathbf{J}^*|^2=J(J+1)$ and J is integral or half integral. In pure case (a) the molecule behaves as a rigid system giving singlets when $\Sigma=0$, doublets when $\Sigma=\frac{1}{2}$ and triplets when $\Sigma=1$. In many important cases $I(\mathbf{L}^*, \mathbf{S}^*)$ is of the form $A_S\overline{L^*S^*\cos(\mathbf{L}^*, \mathbf{S}^*)}$, where[10] the bar indicates an average over all angles, which therefore becomes $A_S\Lambda\Sigma$, where A_S is the sublevel separation in spin multiplets. It is positive in *regular* states and negative in *inverted*. $I(\mathbf{L}^*, \mathbf{ax})$, on the other hand, at least for fixed nuclei, is an even function of $\cos(\mathbf{L}^*, \mathbf{ax})$ which is usually taken as of the form $\overline{A_L L^{*2}\cos^2(\mathbf{L}^*, \mathbf{ax})}=A_L\Lambda^2$. Thus A_L is the separation of a Π and a Σ state which are in the relation of "pure precession" to one another—or are "precessional mates" (i.e., differ only in the average projection of the same **L*** vector). If $A_L>0$ the Π state is above the Σ. Here $A_L>A_S$ but both are large. (See Fig. 1.)

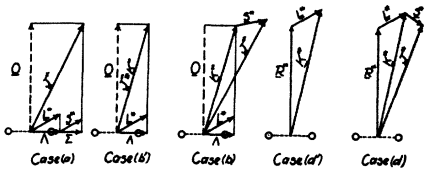

FIG. 1. Hund's coupling cases.

[9] For a more extended account of the coupling cases see Jevon's *Report or Mulliken's Review*, reference 1.

[10] See Hill and Van Vleck, Phys. Rev. **32**, 267 (1928) and Van Vleck, ibid. **33**, 467 (1929). It is useful to use the subscripts S and L for these coupling constants to avoid confusion in what follows.

Hund's case (b′)

This is a special case in which $S=0$ and we have only singlet states. Here as before $I(\mathbf{L}^*, \mathbf{ax})$ remains large and Λ therefore remains as a quantum number. $\mathbf{\Lambda}$ adds vectorially with $\mathbf{O}$ to give $\mathbf{K}^*$ where $|\mathbf{K}^*|=K(K+1)$, $\cdots$ and K is a quantum number representing the total angular momentum of the system, where $K\equiv J=\Lambda$, $\Lambda+1$, $\cdots$. Case (a) reduces to this for singlet states.

Hund's case (b)

This is the general case of which the above is a special one. $I(\mathbf{L}^*, \mathbf{ax})$ remains large while $I(\mathbf{\Lambda}^*, \mathbf{S}^*)$ is negligibly small, due to the feeble magnetic field associated with $\mathbf{\Lambda}$. Consequently Σ ceases to be a good quantum number. As rotation sets in $\mathbf{\Lambda}$ and $\mathbf{O}$ add to give $\mathbf{K}^*$ as before. In this case, however, the magnetic field associated with the direction of $\mathbf{O}$, due to its precession around $\mathbf{K}^*$, gives an average field along $\mathbf{K}^*$ and the interaction of this with $\mathbf{S}^*$, $I(\mathbf{S}^*, \mathbf{K}^*)$, increases in magnitude with K. $\mathbf{S}^*$ is therefore quantized along $\mathbf{K}^*$ its projection taking on the $2S+1$ values determining the multiplicity of the level. $\mathbf{S}^*$ and $\mathbf{K}^*$ compound to give $\mathbf{J}^*$ around which they precess. The sublevels for near case (b) states are designated conventionally F_1, F_2, etc., beginning with the one for which $J=K+S$. Here $I(\mathbf{S}^*, \mathbf{K}^*)$ is a complicated function of $(A_S, \Lambda, K, J-K)$ which for $^2\Sigma$ states gives the simple relation $\gamma(K+\frac{1}{2})$ for the separation of the spin components of doublet level, where $|\gamma| \doteq A_S L_{\text{perp}}$, L_{perp} being the average value (usually small) of the projection of $\mathbf{L}^*$ normal to the axis of figure and A_S is the coupling constant of $\mathbf{L}^*$ and $\mathbf{S}^*$ mentioned above, which in *pure* case (b) of course vanishes.

Hund's case (d′)

In this as in case (b′) above $S=0$ and we have only singlet states. Here, however, $I(\mathbf{L}^*, \mathbf{O})$ is large and $I(\mathbf{L}^*, \mathbf{ax})$ negligible. The period of the precession of $\mathbf{L}^*$ about the axis is now so much smaller than that of the rotation of the nuclei (except of course for no rotation) that the orienting effect of the nuclear axial field cancels over a cycle and Λ no longer exists. The mechanical angular momentum of the revolving nuclei is now quantized and designated by $\mathbf{R}^*$ where $|\mathbf{R}^*|^2=R(R+1)$ and $R=0, 1, 2\cdots$. The interaction of $\mathbf{L}^*$ and the magnetic field along $\mathbf{R}^*$, $I(\mathbf{L}^*, \mathbf{O})$ or $I(\mathbf{L}^*, \mathbf{R}^*)$, is now dominant causing $\mathbf{L}^*$ and $\mathbf{R}^*$ to precess about a quantized resultant $\mathbf{K}^*$. Here K takes on the values $R+L$, $R+L-1$, $\cdots R-L$. In practice of course this gradual uncoupling with the resulting evanescence of Λ as a quantum number begins with the molecule in case (b′) and progresses as rotation increases, the particular one of the $(2L+1)$ limiting cases which is reached being determined by the value of Λ and hence the type of case (b′) state which was the starting point. This will be returned to in more detail later.

Hund's case (d)

This case results when the spin $\mathbf{S}^*$ is added to case (d′). Here $\mathbf{K}^*$ and $\mathbf{S}^*$ have an interaction $I(\mathbf{K}^*, \mathbf{S}^*)$ of the type but in general larger than that in case (b),[11] which causes these vectors to precess about their quantized resultant $\mathbf{J}^*$. Here for each K there are $(2S+1)$—the normal multiplicity—of J-values.

For the purposes of this discussion case (c) coupling is of no significance and will therefore be omitted.

The effect of the field on molecular terms of these limiting types can be predicted in a fairly straightforward fashion by a proper interpretation of Eq. (5). The intermediate types between case (a) and case (b) and between case (b) and case (d) can of course only be discussed by direct quantum mechanics calculations. Where these are not available, the experimental results can none the less be reasonably interpreted in broad outline as intermediate between the simple predictions for the limiting cases concerned.

§4. Zeeman Effect in Singlet Molecular Spectra

A strict case (b′) molecule in a $^1\Sigma$ state possesses no magnetic moment ($\mu=0$) and should therefore be completely *insensitive* to the magnetic field. The absence of any effect in $^1\Sigma$ states has been demonstrated by Watson and Perkins[12] in the $^1\Sigma\rightarrow{}^1\Sigma$ band of AgH at λ3330. In inter-

[11] It of course reduces to the same thing for those case (d) states in which L_{perp}, and hence its average along $\mathbf{K}^*$, vanishes. See section on L-uncoupling later.

[12] Watson and Perkins, Phys. Rev. 30, 592 (1927).

mediate types between case (b′) and case (d′) where L_{perp} takes on appreciable values large effects are to be expected, their magnitude increasing with the uncoupling. These will be considered below.

In $^1\Pi$ and $^1\Delta$ states, on the other hand, $\Lambda=1$ and 2, respectively, and hence $\bar{\mu}=\mu\cos(\mathbf{J}^*,\mathbf{L}^*)=\Lambda\cos(\mathbf{J}^*,\mathbf{\Lambda})=\Lambda^2/[J(J+1)]^{\frac{1}{2}}$. Eq. (5) therefore gives as the magnetic energy W

$$W=M\frac{\Lambda^2}{\sqrt{[J(J+1)]}}\cdot\frac{1}{\sqrt{[J(J+1)]}}\Delta\nu_n=\frac{M\Lambda^2}{J(J+1)}\cdot\Delta\nu_n, \quad (7)$$

or a system of equidistant magnetic sublevels whose separation is directly proportional to H.[12a] Since the number of sublevels is $(2J+1)$ the overall width of the groups decreases approximately as $2\Lambda^2\Delta\nu_n/J$ and therefore becomes very small for large J-values. We see also that the largest separation occurs for $J=\Lambda$ when the outer components are respectively 1 and 8/3 Zeeman units apart.[8] The rapid decrease of the width of magnetic-sublevel groups with J implies at once that the vast majority of lines in singlet bands will show very little effect beyond a broadening, in distinct contrast with the lines of an atomic series.

Now in order to subject such an expression as Eq. (7) to as rigid and complete an experimental test as possible it is desirable to select the most favorable bands available. Determining criteria in such a selection are therefore that the bands shall:

(1) be those of a light molecule to provide as wide a spacing of branch lines as possible; (This practically limits one to hydrides or combinations in the first row of the periodic table.)

(2) involve states which are as rigid as possible (no L-uncoupling);

(3) originate in transitions between a magnetically *insensitive* and a magnetically sensitive state; (This insures that the patterns shall exhibit directly the energy splitting of a single state and limits the choice to $\Pi\rightarrow\Sigma$ or $\Sigma\rightarrow\Pi$ transitions.)

(4) be in a region open to work in air with rapid plates and

(5) capable of reasonably intense excitation and free from extraneous band systems.

These restrictions limit the field so greatly that practically only the $^1\Sigma\rightarrow{}^1\Pi$ bands of He_2, the $^1\Sigma\rightarrow{}^1\Pi$ Angstrom bands of CO and the $^1\Pi\rightarrow{}^1\Sigma$ bands of AlH are available.

[12a] This, in a different notation, is the result obtained by Van Vleck, reference 7.

$^1\Sigma\rightleftarrows{}^1\Pi$ bands

In the case of the Angstrom bands of CO five have been examined in detail[13] over a series of field strengths up to 36,000 gauss.

Since in bands of this type the magnetic sublevels of the $^1\Pi$ state (the other having a $(2J+1)$-fold degeneracy) decrease so rapidly in separation with J there is little experimental hope of actually resolving more than a few of the simpler patterns. It consequently becomes desirable to calculate in addition the *intensities* involved so that partially resolved patterns can at least be compared qualitatively with the theoretical expectations. Now these can be computed from the intensity formulae deduced by Kronig[13a] and Hönl[14] which are in harmony with those obtained by Dennison[15] for the Zeeman components of the spectrum lines of a rigid symmetrical rotator and are given in a convenient form in reference 12. These may be written in our notation,[16]

$$\left.\begin{array}{lll} P\text{ branch} & I_0=\dfrac{3(J^2-M^2)(J+1)}{(2J-1)(2J+1)J} & \parallel \\ & I_{\pm1}=\dfrac{3(J\pm M)(J\pm M-1)(J+M)}{4J(2J-1)(2J+1)} & \perp \\ Q\text{ branch} & I_0=\dfrac{3M^2}{J(J+1)} & \parallel \\ & I_{\pm1}=\dfrac{3(J\pm M)(J\mp M+1)}{4J(J+1)} & \perp \\ R\text{ branch} & I_0=\dfrac{3[(J+1)^2-M^2]J}{(J+1)(2J+1)(2J+3)} & \parallel \\ & I_{\pm1}=\dfrac{3(J\mp M+1)(J\mp M+2)J}{4(J+1)(2J+1)(2J+3)} & \perp \end{array}\right\} \quad (8)$$

[13] Kemble, Mulliken and Crawford, Phys. Rev. **30**, 438 (1927); Crawford, ibid. **33**, 341 (1929).

[13a] R. de L. Kronig, Zeits. f. Physik **31**, 885 (1925).

[14] Hönl, Zeits. f. Physik **31**, 340 (1925); Hönl and London, Zeits. f. Physik **33**, 803 (1925).

[15] Dennison, Phys. Rev. **28**, 318 (1926).

[16] In Eq. (9B) of reference 12 the second $\pm$ sign should read $\mp$.

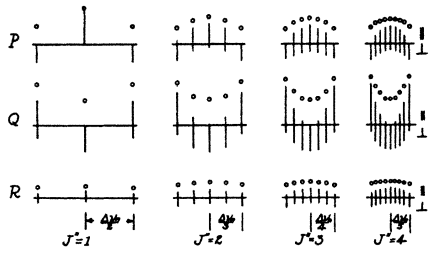

FIG. 2. Zeeman patterns in $^1\Sigma \rightarrow {}^1\Pi$ transition. The patterns for the first four lines of the P, Q and R branches are shown, the pattern sizes being computed from Eq. (7) and the component intensities from Eq. (8). The intensities for polarization parallel (||) to H (transverse observation) are plotted upward, those for perpendicular polarization ($\perp$) downward, while both intensities superposed are given by the vertical distance of the circles. The same diagrams would of course apply to a $^1\Pi \rightarrow {}^1\Sigma$ transition except that J would now refer to the initial value, J'. The pronounced doublet-like character of the Q lines in parallel polarization is particularly characteristic and observable for large values of J''.

where J and M are the *final* values in all cases and the I_0 and $I_{\pm 1}$ correspond to $\Delta M = 0$ and ± 1, respectively. Here I_0 corresponds to parallel (||) polarization (observation transverse to the field) and $I_{\pm 1}$ to perpendicular ($\perp$) polarization. In general due to the lack of splitting in the upper state I_{+1} and I_{-1} must be added for a given value of M for $\perp$ components. Fig. 2 shows these intensities for the first four lines of the P, Q and R branches as plotted from Eqs. (8) (which involve the proper relative intensities of the lines in a band but of course do not include Boltzmann factors). Since the first lines in a branch are the faintest the intensities of the Zeeman components are further reduced so that experimental study of the most important patterns involves very protracted exposures. It will be observed that the Q lines in || polarization should give patterns having zero intensity at the center and the greatest at the edges, while the P lines should have the greatest intensity at the center and the least at the edges. The behavior of the Q and P lines in $\perp$ polarization is reversed. The R lines are intermediate between the P and Q, though more closely resembling the former.

Experimentally it has been possible to resolve patterns only for $J''=1$ and $J''=2$. Of the 18 possible patterns thus obtainable (counting ||, $\perp$ and both superposed as three different cases) 13 were resolved into separate components. The location of the components agreed closely with the theoretical patterns at moderate fields, though the pattern widths were slightly too small at the highest fields. They seemed in all cases to be symmetrical around the no field positions. The departure from linearity at the highest fields is quite definite and is presumably due to the fact that the very high fields are just beginning to distort the CO molecule appreciably. Further evidence of distortion is furnished by the fact that the *intensities* of the components which at low fields are sensibly symmetrical, grow more asymmetric as H increases. These asymmetries increase as J increases and are opposite in character for a Q and a P line. Thus the *low* frequency components of a Q line in || polarization and of a P line in $\perp$ polarization are relatively more intense; conversely the *high* frequency components are relatively strengthened for Q lines in $\perp$ and P lines in || polarization. Kronig[17] showed that this was due to the perturbing action of the field on the transition probabilities involved, that to a first order approximation the asymmetry should increase as the field and what components on one side of the pattern gained the others should lose. This seems to be in complete qualitative harmony with the observations.

It was further found that qualitatively the gross features of the patterns for $J''>2$ were in excellent agreement with the expectations. In particular the doublet-like patterns could be traced in the P-branch ($\perp$) as high as $J''=10$ or 12 and in the Q-branch (||) where the central components should be fainter, as high as $J''=16$. The small broadening due to the field could be traced almost to the end of the branches. The overall widths while not very sharply defined were definitely just under the extreme widths predicted by Eq. (7).

It thus appears that the theoretical expectations are verified *qualitatively* to the smallest details and *quantitatively* in all essential features. In the case of other bands of this sort Watson and Perkins[18] have studied a $^1\Pi \rightarrow {}^1\Sigma$ band of AlH at $\lambda 4240$ and Curtis and Jevons[18a] several

[17] Kronig, Phys. Rev. **31**, 195 (1928).

[18] Watson and Perkins, Phys. Rev. **30**, 592 (1927).

[18a] Curtis and Jevons, Nature **116**, 746 (1925); Proc. Roy. Soc. **A120**, 110 (1928).

$^1\Pi \rightarrow {}^1\Sigma$ bands of helium. Though in neither case was sufficient dispersion available for resolution of even the widest patterns the observed broadenings and their variation in different polarizations are in accord with theory.

No observations on bands involving a $^1\Delta$ state have been made though if the λ3260 band of NH ($^1\Pi \rightarrow {}^1\Delta$) could be excited with sufficient intensity it should give some interesting results.

§5. Zeeman Effect in Multiplet-Spectra (Pure Case (a) and Case (b))

The behavior of multiplet molecular terms in the magnetic field is determined by the nature of the couplings involved. If we have a pure case (a) molecule both $\mathbf{L}^*$ and $\mathbf{S}^*$ precess about the internuclear axis to give projections Λ and Σ whose sum Ω is unaffected by either rotation or external magnetic fields. Since Σ has twice the magnetic moment associated with it that Λ has this gives $m=\Lambda+2\Sigma$ where $|\mu|=m$ Bohr magnetons and μ is always along the nuclear axis. When rotation of the molecule sets in, however, the components of μ $\perp$ to the axis of rotation cancel over a cycle leaving as the average $\overline{m}$ of the magnetic moment along $\mathbf{J}^*$,

$$\overline{m}=m\cos(\mu,\mathbf{J}^*)=\frac{(\Lambda+2\Sigma)\Omega}{J^*}=\frac{(\Omega+\Sigma)\Omega}{\sqrt{[J(J+1)]}}.$$

Consequently from Eq. (5)

$$W=\frac{M(\Omega+\Sigma)\Omega}{J(J+1)}\Delta\nu_n, \tag{9}$$

which, when there is no spin present, reduces of course to Eq. (7) for case (b′). The results to be expected for various types of case (a) and case (b′) states are summarized in Table I. In each case the number of magnetic sublevels is $(2J+1)$ and they are *equally* spaced, the spacing being represented as multiples of $\Delta\nu_n/J(J+1)$.

It is to be noted that all $^2\Pi_{1/2}$ and $^3\Delta_1$ states should be magnetically insensitive since the magnetic moments of Λ and Σ cancel exactly. In the case of $^3\Pi_0$ states we have the same result due to the fact that here the *mechanical* momentum of Λ and Σ cancel, thus causing $\mathbf{J}^*$ to be along the axis of rotation. Consequently the magnetic moment, which is $(\Lambda+2\Sigma)=-1$ and is $\perp$ to $\mathbf{J}^*$ is averaged out completely over a cycle.[19] (See Fig. 3 and Fig. 4.)

Table 1. *Separations in case (a) and case (b′) states.*

State	Nature of J	Separation of sublevels	Number of sublevels
$^1\Pi$ $^1\Delta$	integral	1 4	odd
$^2\Pi_{1/2}$ $^2\Pi_{3/2}$	half integral	magnetically insensitive 3	even
$^2\Delta_{3/2}$ $^2\Delta_{5/2}$	half integral	1 5/2 3/2	even
$^3\Pi_0$ $^3\Pi_1$ $^3\Pi_2$	integral	magnetically insensitive 1 6	odd
$^3\Delta_1$ $^3\Delta_2$ $^3\Delta_3$	integral	magnetically insensitive 4 12	odd

In the case of pure case (b) states on the other hand, for *low* states of rotation in general and for *all* states when the spin-doubling, trebling, etc., is negligible, the electronic spin vector orients itself with respect to the field independently of the rest of the molecule. The rest of the molecule behaves as in case (b′) and we have the molecular analogue of the Paschen-Back effect, $\mathbf{S}^*$ and $\mathbf{K}^*$ being quantized separately along the field, the new quantum numbers being $M_k=K,\ K-1\cdots K$ and $M_S=S,\ S-1,\ \cdots S$. We can therefore write the total energy in the magnetic field as the sum of *two* terms of the type of Eq. (5):

$$\Delta W=\frac{M_k\Lambda^2}{K(K+1)}\Delta\nu_n+2M_S\Delta\nu_n$$
$$=\left(\frac{M_k\Lambda^2}{K(K+1)}+2M_S\right)\Delta\nu_n. \tag{10}$$

For doublet states therefore we expect two subgroups of magnetic levels each symmetrical about positions $\pm\Delta\nu_n$ removed from the no field position. Moreover as K increases these subgroups contact in total width as $1/(K+1)$ whereas the separation of their centers of gravity remains fixed at $2\Delta\nu_n$. For triplet states similarly

[19] When no nuclear rotation is present, i.e., in the lowest state, and we have the analogue of atomic $^2P_0$ states which are *insensitive* to the field.

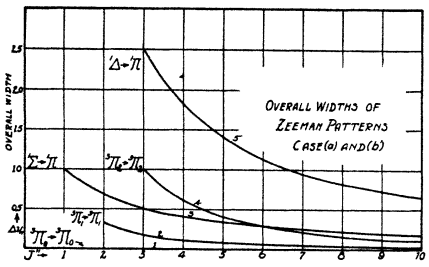

FIG. 3. Overall width of Zeeman patterns (case (a) and case (b')). For purposes of comparison the overall widths of the pattern for a $^1\Sigma \rightarrow {}^1\Delta$ transition (any branch, either polarization), $^1\Delta \rightarrow {}^1\Pi$ and $^3\Pi \rightarrow {}^3\Pi$ transitions (P branches and $\perp$ polarization) are plotted against J''. Curves 3 and 5 would hold equally well for case (b) coupling and multiplet states where the spin multiplicity is of negligible magnitude. Curves 1, 2 and 4 assume pure case (a) coupling and would reduce to curve 2 in the case of pure case (b) coupling and complete spin Paschen-Back effect.

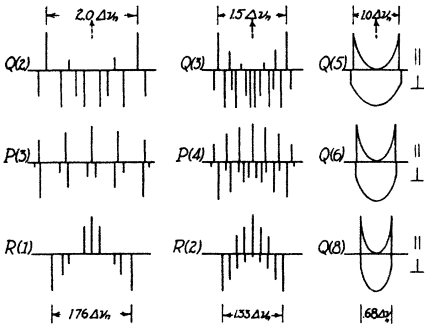

FIG. 4. Zeeman patterns of early lines in $^1\Delta \rightarrow {}^1\Pi$ transitions. A few of the patterns to be expected for a $^1\Delta \rightarrow {}^1\Pi$ transition are given, both states being case (b'). The dotted arrows indicate the zero-field positions. The computed intensities (reference 70) as in Fig. 2 are plotted *above* and *below* the horizontal lines for || and $\perp$ polarizations, respectively. They do not include corrections for the relative intensities of the lines (as a whole) in a band but nevertheless are of great assistance in interpreting the experimental data. They of course apply equally to $^3\Delta \rightarrow {}^3\Pi$ transitions in which the spin trebling is negligible, and were so applied by Mills in a study of the ortho-helium bands where the structure of the bands indicated case (b') coupling in both states. The agreement between the theoretical and observed patterns was good.

we have three such subgroups—the center of the middle one at the no field position and that of the other two $\pm 2\Delta\nu_n$ from this position. For large K therefore we have a somewhat unsharp triplet of total width $4\Delta\nu_n$.

Multiplet Σ states are always case (b) for the lowest K values at least and provided the spin multiplet separation can be neglected are so in general. We obtain therefore, according as $S=\frac{1}{2}$ or 1, simply doublet levels of separation $2\Delta\nu_n$ or triplet levels of total width $4\Delta\nu_n$, independent of the value of K. (In practice the growing importance of $I(\mathbf{K}^*, \mathbf{S}^*)$ gradually broadens these sharp levels as will appear later.)

Doublet spectra

The great majority of known molecular states must be classified as intermediate between case (a) and case (b). If we consider for the time only doublet states without rotation the separation of the members of the electronic doublet (such as $^2\Pi_{3/2}-{}^2\Pi_{1/2}$ or $^2\Delta_{5/2}-{}^2\Delta_{3/2}$) is determined by $I(\mathbf{S}^*, \mathbf{ax})$ or in this case simply A_S. If then B is the usual rotation energy constant $(h/8\Pi^2cI)$ (I = moment of inertia), as Hill and Van Vleck[19a] and Mulliken[20] have shown the whole range of intermediate couplings can be characterized by the value of A_S/B which we shall refer to as Y (rather than λ as used by Hund V.V.). Here pure case (a) *regular* corresponds to $Y=+\infty$ case (a) *inverted* to $Y=-\infty$ and $Y=0$ or $+4$ to case (b). Only near these limiting ranges therefore may we expect the simple results expressed in Eqs. (9) and (10) to give an adequate description of the facts. Now of all the molecules which have been examined in the field (see Fig. 5) it appears that the closest approach to rigid case (a) states are found in the prominent doublet bands of CaF, SiF, BaF, CaCl and BaCl, bands which offered the first experimental demonstration of the effect of magnetic fields on molecular spectra. (Here each

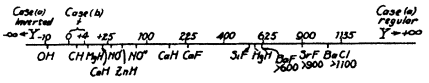

FIG. 5. Values of $Y=A_S/B$ for $^2\Pi$ states of molecules which have been studied in the field. They are plotted against a square root scale. The limits for BaF, SrF and BaCl are estimated from the fact that the Y-values must be $201/B$, $279/B$ and $373/B$, respectively, and the B-values are certainly smaller than that of CaF which is 0.32. (See Mulliken and Christy, Phys. Rev. **38**, 87 (1931).)

[19a] Hill and Van Vleck, Phys. Rev. **32**, 261 (1928).

[20] Mulliken, Review IIb; Mulliken and Christy, Phys. Rev. **38**, 87 (1931).

of the band systems, is attributed to a $^2\Pi \rightarrow {}^2\Sigma$ transition.) In the case of only the first two is $Y=A/B$ known, where we have respectively $75/0.32=230$ and $156/0.29=540$. For the others fine structure analysis is not possible due to the smallness of B. On the other hand, we should have for CaCl, $Y=70/B$, BaF, $Y=201/B$, and BaCl, $Y=373/B$, where on general grounds we should expect the B's to be certainly smaller than 0.3. Hence the values of Y are quite large and the molecules accordingly in the Π states should be quite rigid. Moreover in all of these cases the moments of inertia are so nearly alike in the upper and lower states that the branches which form the heads turn back on themselves at very large J values indeed. Hence any observable Zeeman effect could only result from the splitting of the lower $^2\Sigma$ state into two (slightly diffuse) states, $2\Delta\nu_n$ apart. The single subheads should therefore become *double* heads of roughly this separation, which is precisely what Dufour[21] observed. Actually of course the results cannot be clear cut since we have such closely packed lines at the head and are neglecting the spin doubling in the $^2\Sigma$ states (see below). Later E. von Mathes[22] examined in detail the fluoride bands of Ca, Sr and Ba and confirmed this result very clearly. Her results on the $^2\Sigma \rightarrow {}^2\Sigma$ bands of CaF at λ5292, etc., in striking contrast, as one might expect showed only broadening in the field and no visible structure.

Triplet spectra

In triplet states ($S=1$) with $\Lambda \neq 0$ where the coupling approaches that of case (a) we should expect the magnetic levels to be given by Eq. (9), and therefore rather large effects for low values of J. The only bands involving such a state which have been studied are the first positive bands of N_2 ($^3\Pi \rightarrow {}^3\Sigma$) studied by Croze[23] who reports results on the heads only, of five bands of the $\Delta v=-4$ progression. It is probable that these are the $^3\Pi_0 \rightarrow {}^3\Sigma$ subheads since these lie to the red and the bands degrade toward the violet. These all give triplets, quite unsymmetrical in intensity but of total width averaging $3.99\Delta\nu_n$. If now the $^3\Pi_0$ state is near enough case (a)[23a] to be relatively insensitive for the values of J involved and we have a complete Paschen-Back effect in the $^3\Sigma$ state (which should be true for moderate fields) triplets of $4\Delta\nu_n$ is precisely what we should expect. (The data and observations on the other heads are rather indefinite and merely indicative of *some* effect.) Similar results have been reported by Schmid[24] for a third-positive carbon band (λ2978) involving a $^3\Sigma \rightarrow {}^3\Pi$ transition. Here (although the rotational analysis is not completed) the $^3\Pi$ state is between case (a) and case (b), but since the subheads are clearly visible must be fairly near case (a) for such intermediate values of J. In the field therefore we are not surprised to find fairly definite triplets of about the expected width, $4\Delta\nu_n$, due to nearly complete Paschen-Back effect in the upper state.

In the case of the second positive N_2 bands ($^3\Pi \rightarrow {}^3\Pi$) although a number of observers have photographed them in the field the results are rather fragmentary. In general—if both states were case (a)—after the first few lines we should expect even smaller broadening than for the corresponding lines of a $^1\Sigma \rightarrow {}^1\Pi$ band due to the almost complete cancellation of the magnetic displacement in one level by that in the other. (See Fig. 3). No results have been obtained for the early lines though Fortrat[24a] who has used fields up to 49,000 gauss finds that the higher triplets show a definite *contraction* varying as H^2, the contraction being of the order of one-seventh $(\Delta\nu_n)^2$.

The C_2 swan bands ($0 \rightarrow 0$ band at λ5165) are also due to a $^3\Pi \rightarrow {}^3\Pi$ transition and are similar

[21] Dufour, C. R. **146**, 118, 229, 810 (1908); Ann. de Physique **9**, 409 (1908); Le Radium **5**, 291 (1908); J. de Physique **8**, 237 (1909); Zeits. f. Physik **10**, 124 (1910). Also Fabry: C. R. **138**, 158 (1) (1904); C. R. **140**, 578 (1908).

[22] von Mathes, Zeits. f. Physik **68**, 493 (1931).

[23] Croze, Ann. de Physique **1**, 63 (1914).

[23a] The separations of the electronic spin levels here are $^3\Pi_2-{}^3\Pi_1=+40$ cm^{-1} and $^3\Pi_1-{}^3\Pi_0=+37$ cm^{-1} and are thus not equal as they should be for a case (a) state. They are however much larger than $\Delta\nu_n$ and remain so with increasing J. See Naudé, Phys. Rev. **38**, 372 (1931); Proc. Roy. Soc. **A136**, 114 (1932).

[24] Schmid, Phys. Rev. **39**, 539 (1932).

[24a] Fortrat, Ann. de Physique **3**, 345 (1915). See also Deslandres and D'Azambuja C. R. **158**, 153 (1914). Photographs taken by the author—preliminary to a study of the Zeeman effect near perturbations—have shown that up to 25,000 gauss or so the higher lines are slightly contracted—with the outer members somewhat less sharp than the central member of a triplet (R_2 branch lines).

to the second positive of N_2, except that for each state case (b) coupling is approached much more closely at moderate J values with the result that the two groups of triplets formed by the P_1, P_2 and P_3 lines and the R_1, R_2 and R_3 lines eventually become very narrow at large J values. The effect of high fields is therefore in both states to give triplet levels broadened by the residual interaction $I(\mathbf{K}^*, \mathbf{S}^*)$. The selection rule $\Delta M_S=0$ as the Paschen-Back condition is approached, is now more and more rigorously obeyed. Consequently we expect the triplet structure of the no field lines to be destroyed as the field is increased the individual lines becoming broader until only a band of the general width of the original narrow triplet is left. This seems to be essentially what is observed by Deslandres and Burson[25] and by Fortrat[24a, 26] for the narrower triplets. The widest triplets merely show a slight broadening of the individual members and a small contraction in separation of the outer pair, as in the corresponding N_2^+ doublet bands. This second order contraction of spin multiplets is a very general phenomena and can be accounted for in a quantitative manner in the case of *doublet* spectra. (Cf. CN and N_2^+ below.)*

In the ortho-helium (He_2) bands we have the best known example of triplet bands in which the spin trebling is so small (of the order of a few tenths of a wave number only) that an almost complete Paschen-Back effect is attained for all fields of usable magnitude. We have consequently three fairly sharp substates given by the term ${}^2M_S\Delta\nu_n$ ($M_S=0, \pm1$) in Eq. (10) which are symmetrical around the center of gravity of the no-field (unresolved) triplet and $2\Delta\nu_n$ apart and superposed on these the patterns given by the first term. With the selection rules $\Delta M_S=0$, $\Delta M_k=0, \pm1$ we expect therefore patterns which for ${}^3\Pi\rightarrow{}^3\Sigma$ transitions, for example, are indistinguishable from those of the corresponding singlet transitions. Thus Curtis and Jevons[27] have found patterns in several orthohelium bands due to ${}^3\Pi\rightarrow{}^3\Sigma$ and ${}^3\Sigma\rightarrow{}^3\Pi$ transitions which were identical with the corresponding patterns obtained in parahelium (${}^1\Pi\rightarrow{}^1\Sigma$) bands. Likewise Mulliken and Monk[28] in the λ6400 band ($3s\sigma\,{}^3\Sigma\rightarrow 2p\pi\,{}^3\Pi$) have obtained results even for the lowest fields which they used (10,000 gauss) in complete harmony with ${}^1\Sigma\rightarrow{}^1\Pi$ predictions (cf. Fig. 2).

A more extended series of measurements on orthohelium has been made by Mills[29] in the $nd\sigma\,{}^3\Sigma\rightarrow 2p\pi\,{}^3\Pi$ and $nd\delta\,{}^3\Delta\rightarrow 2p\pi\,{}^3\Pi$ bands ($n=3$, 4). In both cases the agreement with case (b′) predictions—where of course Eqs. (7) and (10) give identical patterns—was good. In the ${}^3\Delta\rightarrow{}^3\Pi$ bands the patterns are qualitatively similar to those of a ${}^1\Pi\rightarrow{}^1\Sigma$ transition except that now with $\Lambda=2$ in the upper state the patterns are much wider at the beginning and continue to be appreciable much farther along in each branch. A few of the more striking patterns are sketched in Fig. 4 (after Mills) which should be compared with Fig. 2. The pronounced doublet-like patterns in the Q lines (||) could be followed to quite high K values as in the analogous case in CO. For purposes of comparison Fig. 5 shows as a function of K, among others, the overall width of $\Delta\rightarrow\Pi$ patterns. This curve holds equally well for singlet bands or multiplet case (b) bands with complete Paschen-Back effect in both states.

§6. Zeeman Effect in ${}^2\Sigma$ States and ${}^2\Sigma\rightarrow{}^2\Sigma$ Bands

We have seen that in a ${}^2\Sigma$ state in which $I(\mathbf{K}^*, \mathbf{S}^*)$ is small the field is able to overcome this coupling completely with the result that the spin, $\mathbf{S}^*$, is quantized separately in the field, with $M_S=\pm\frac{1}{2}$. The two levels although having a $(2K+1)$ fold degeneracy due to the possible orientations of $\mathbf{K}^*$, are none the less sharp, and therefore since only transitions with $M_S'=\frac{1}{2}\rightarrow M_S''=\frac{1}{2}$ and $M_S=-\frac{1}{2}\rightarrow M_S''-\frac{1}{2}$ are allowed, each line of such a ${}^2\Sigma\rightarrow{}^2\Sigma$ band is undisplaced and shows no Zeeman effect whatsoever. Since,

[25] Deslandres and Burson C. R. **158**, 1851 (1914).

[26] Fortrat, C. R. **156**, 1459 (1913).

* *Note added in proof.* H. Batsch working on the NH bands at $\lambda\lambda$3360 and 3370 which are assigned to a ${}^3\Pi\rightarrow{}^1\Sigma$ transition finds that the field causes a contraction of the triplets involved which varies closely as H^2. For details, see Ann. d. Physik **18**, 81 (1933).

[27] Curtis and Jevons, Nature **116**, 746 (1925); Proc. Roy. Soc. **A120**, 110 (1928).

[28] Mulliken and Monk, Phys. Rev. **34**, 1530 (1929).

[29] Mills, Phys. Rev. **37**, 1005 (1931); **38**, 1148 (1931).

however, $I(K^*, S^*)$ produces a spin doubling which increases linearly with K, in fact as $\gamma(K+\frac{1}{2})$, where γ is usually small, one may expect that for large enough K this spin doubling will be of the order of the value of the $\Delta\nu_n$ involved and the situation ceases to be so simple. If we imagine for a given K that γ is allowed to increase, its effect will at first simply be to broaden slightly the originally sharp levels with $M_S=\pm\frac{1}{2}$, the broadening being of the order of magnitude of the no field spin doubling. On the contrary, for very large values of γ each substate of the spin multiplet ($J_1=K+\frac{1}{2}$, $J_2=K-\frac{1}{2}$) behaves as a rigid system in the field assuming $(2J+1)$ orientations in the field. The extreme members of each group of magnetic levels, since $\mathbf{S}^*$ has a constant projection parallel or antiparallel to $\mathbf{K}^*$ of $\frac{1}{2}$ unit, will lie $2\Delta\nu_n$ apart and be symmetrical about the no field energy position. For values of γ such that $\gamma(K+\frac{1}{2})\approx\Delta\nu_n$ for the field being considered resort must be had to precise calculations.

On the assumption of case (b) coupling of the electron spin and considering the only significant perturbation energy in the field to be that due to the interaction of $\mathbf{S}^*$ and the field $\mathbf{H}$, Hill[30] has deduced a quantum mechanical expression for the energy of a $^2\Sigma$ state molecule in the field which holds for the whole range of spin-coupling values considered above. The expression for the energy, W, is

$$W=\pm\tfrac{1}{2}\{\nu^2+4M\nu\Delta\nu_n/(K+\tfrac{1}{2})+4\Delta\nu_n^2\}^{\frac{1}{2}} \quad (11)$$

where now W is the energy of the molecule in the field measured from the *midpoint* of the no field spin states and hence includes $\pm\frac{1}{2}\nu$, where ν is the doublet level separation $\gamma(K+\frac{1}{2})$, in addition to the magnetic energy involved. Here the *upper* sign goes with the $J=(K+\frac{1}{2})$ state (which corresponds in the normal case to the energetically *higher* of the pair of spin states) and the lower sign with the $J=K-\frac{1}{2}$ state. The two extreme magnetic levels for the $J=K+\frac{1}{2}$ state, where $M=\pm(K+\frac{1}{2})$, need separate treatment since the energy determinant of which Eq. (11) gives the roots now reduces to a single term. The roots of this term are

$$W=\tfrac{1}{2}\nu\pm\Delta\nu_n, \quad (12)$$

which therefore shows that the block of magnetic sublevels for the $J=K+\frac{1}{2}$ level at least, is always $2\Delta\nu_n$ in width, as was suggested above for the two limits of very small and very large spin doubling.

The general features of the energy level diagrams as computed from Eqs. (11) and (12) are shown in Fig. 7 where the doublet separation is taken as 0.22 $(K+\frac{1}{2})$, that of the $^2\Sigma$ state of OH, and $H=20{,}000$ gauss. Here the dashed lines represent the no-field positions and the sublevels are distributed fairly uniformly for the upper level between the curves marked $M=\pm(K+\frac{1}{2})$ and for the lower level between those marked $M=\pm(K-\frac{1}{2})$. The curves for $M=0$ of course correspond to no real levels (J half integral) but serve the useful purpose of dividing the total *number* of sublevels into equal groups. Due to the peculiar "crossing over" effect of the $M=-(K+\frac{1}{2})$ level,—curves are also drawn for $M=\pm(K-\frac{1}{2})$ (upper member, $J=K+\frac{1}{2}$). This diagram shows very clearly the passage from almost complete Paschen-Back effect for $K=1$ to the fairly symmetrical groups of sublevels resulting when the spin is tightly coupled to the $\mathbf{K}^*$ vector. It will be considered again in connection with $^2\Sigma\rightarrow{}^2\Pi$ transitions. Unless one proceeds, however, to the rather tedious calculation of the intermediate sublevels it is difficult to foresee certain effects which are largely masked in $^2\Sigma\rightarrow{}^2\Pi$ transitions and yet which are the *only* Zeeman effects in many $^2\Sigma\rightarrow{}^2\Sigma$ transitions. Reference is here made to the contraction of spin doublets in the magnetic field—an effect rather hard to read directly from Eq. (11)—and yet one which seems to be a characteristic of all narrow spin doubling in molecular spectra.

In the violet CN ($^2\Sigma\rightarrow{}^2\Sigma$) bands we have in each case a single P and single R branch which at high values of K begin to show a small scale doubling which increases at first nearly linearly with K. In the magnetic field these doublets show a contraction (the individual lines becoming at the same time somewhat broader) which has been studied by Deslandres and Burson,[31] by Fortrat[32] and in more detail by Bachem.[33] If n represents

[30] This result was first published by Almy, Phys. Rev. **35**, 1495 (1930).

[31] Deslandres and Burson, C. R. **157**, 1105 (1913).

[32] Fortrat, C. R. **158**, 334 (1914).

[33] Bachem, Zeits. f. Physik **3**, 372 (1920).

the no-field separation of these narrow doublet lines ($=(\gamma'-\gamma'')(K+\frac{1}{2})$) and δn the contraction observed in the field Fortrat has shown that for low fields his results can be expressed by the relation

$$n\delta n/H^2=\text{constant}=\alpha \tag{13}$$

where α was sensibly the same for R and P lines the same distance from the origin and decreased slowly with K. This α he termed the "sensitivity" of the doublet to the field. Bachem showed that actually the sensitivity decreased slowly with the field and that his extensive results were represented quite accurately by

$$n\delta n/(1-\delta n/n)=\alpha H^2, \tag{14}$$

which for not too great fields becomes

$$n\delta n=\alpha H^2(1-\alpha' H^2\cdots), \tag{15}$$

where $\alpha'=\alpha/n^2$. Eq. (14) of course predicts that complete contraction of the doublets will not be attained at finite fields—although due to the simultaneous broadening of the individual components doublet structure should vanish at fields for which Eq. (14) would still predict finite separation. Here α and α' both decrease with K (K from 64 to 95), but average around 1.7 $\times10^{-9}$ for the former and 6.5×10^{-9} for the latter.

Now as the following examination will show an expression of the same analytic form as Eq. (15) follows directly from Eq. (11)—where, however, a more complicated dependence of α' on α and n results.

If we confine ourselves to low fields and large values of K, Eq. (11) may be, for both levels of CN, expanded on the assumption that $\nu\gg\Delta\nu_n$. If we neglect the difference between K and $K\pm\frac{1}{2}$ and write $k=2M/K$ and $y=2\Delta\nu_n(=9.3410^{-4}H)$ we may write Eq. (11)

$$W=\pm\tfrac{1}{2}\nu[1+(y/\nu)(k+y/\nu)]^{\frac{1}{2}} \tag{16}$$

or expanding

$$W=\pm\tfrac{1}{2}\left[\nu+\tfrac{1}{2}ky+\tfrac{1}{2}\left(1-\frac{k^2}{4}\right)\frac{y^2}{\nu}\right. \tag{17}$$
$$\left.-\tfrac{1}{4}\left(1-\frac{k^2}{4}\right)\frac{ky^3}{\nu^2}-\frac{1}{128}(16-24k^2+5k^4)\frac{y^4}{\nu^3}+\cdots\right].$$

Hence if ν' and ν'' (we shall assume that $\nu'>\nu''$, see Birge[34]) represent the spin separation in the initial and the final levels, W' and W'' the corresponding energies, $W'-W''\mp\frac{1}{2}(\nu'-\nu'')$ is the displacement of a given Zeeman component from its parent line, and therefore corresponds to a contraction when this quantity is negative. But from Eq. (17) we can write

$$W'-W''\mp\tfrac{1}{2}(\nu'-\nu'')$$
$$=\pm\tfrac{1}{2}[ay+by^2+cy^3+dy^4+\cdots], \tag{18}$$

where the coefficients a, b, c, d, etc., have values determined by ν', ν'', K', K'', M' and M''. Here for such large K-values $K\approx K\pm1$ and hence $K'\approx K''$ and no appreciable differences between P and Q lines are expected. Also in general $M'\rightarrow M''\pm1$, or $M'\rightarrow M''+0$ and components with $\Delta M=+1$ and $\Delta M=-1$ may be expected to be fairly close to and nearly if not quite symmetrical around the component with $\Delta M=0$, $M\rightarrow M$. Since we are primarily concerned with centers of gravity of unresolvable components we shall then consider $M'=M''=M$. Furthermore all the terms in the odd powers of the field ($y\propto H$) are odd also in k and hence in M. The displacements contributed by the *odd* powers are therefore symmetrical about $M=0$ and since they contain M as a factor they vanish for $M=0$. As a result—as far as their effect on the appearance of a complicated unresolved pattern is concerned—with M both positive and negative they produce a broadening but no shift of the center of gravity of the pattern. The *even* powered terms on the contrary involve even powers of M only and do *not* vanish with M. They produce therefore not only a broadening but a *shift* since now components of the same $|M|$ will coincide and the allowed components in the more significant terms will be distributed parabolically between their position for $M=0$ and $|M|=K$. But this means that they will be most dense for M near zero. Now b in Eq. (18) contains the factor $(1-M^2/K^2)$ which is unity for $M=0$ and vanishes for $M=K$. If we assume that all the components are of the same intensity (which is a reasonable approximation for such large K values) and form

[34] Birge, Bull. Nat. Res. Council, p. 182. It is now pretty certain that γ in the lower state is *not* zero. See Jenkins, Roots and Mulliken, Phys. Rev. 39, 16 (1932).

a continuous parabolic distribution, the center of gravity should be near $M=0.34K$. With this value of M inserted in Eq. (18) in the even powered coefficients and $M=0$ in the odd, we can identify the left-hand side as approximately $\frac{1}{2}\delta n$ the actual displacement of the center of gravity of either member of the doublet from its zero position. Hence to fourth powers in the field.

$$\tfrac{1}{2}\delta n=\pm\tfrac{1}{2}[by^2+dy^4+\cdots]=\pm\tfrac{1}{2}\left[0.43\frac{\nu''-\nu'}{\nu'\nu''}y^2-0.047\frac{\nu''^3-\nu'^3}{\nu'^3\nu''^3}y^4\cdots\right]. \tag{19}$$

But $\nu''<\nu'$ and the second term is small compared to the first. Hence $\delta n/2<0$ for the high frequency component (upper sign) and >0 for the low frequency component (lower sign). Hence each component is shifted towards the center and $|\delta n|$ represents the actual contraction to be expected. So we may write (dropping the absolute value sign for convenience) for $n\delta n$

$$n\delta n=0.43\frac{n(\nu'-\nu'')}{\nu'\nu''}y^2\left[1-0.11\frac{(\nu'^3-\nu''^3)}{(\nu'-\nu'')\nu'^2\nu''^2}y^2+\cdots\right] \tag{26}$$

which is of the general form of Eq. (15) since $y=2\Delta\nu_n\propto H$. Further the coefficients in Eq. (26) vary in the same general way with K as do α and α' of Eq. (15). On the quantitative side, unfortunately, the precise values of ν' and ν'' are unknown for such large values of K. Further either one or both is varying in a nonlinear fashion with K since the no field doublets attain a maximum separation near $K=75$ and decrease thereafter. If as an estimate[34] we take $\nu''=0.009K$ and write $\nu'=n+\nu''$ we have from Eq. (26)

$$\frac{n\delta n}{H^2}=\frac{387n^2\cdot10^{-9}}{(n+0.009K)K}\left[1-\frac{0.95\times10^4(n^2+0.027K+3\times10^{-4}K^2)}{K^2(n^2+0.018K+10^{-4}K^2)}10^{-9}H^2\right] \tag{27}$$

which gives the following values (for $K=74$ and $K=90$) of $n\delta n/H^2$,

K	2000	4000	5000 (H in gauss)
74	1.14	1.09	1.06
	(1.60)	(1.53)	(1.51)
90	0.84	0.82	0.80
	(1.42)	(1.38)	(1.30)

where the values in parenthesis are those measured by Bachem. The agreement as to order of magnitude and general trend is probably as good as could be expected in view of the extreme sensitivity of the theoretical coefficients to variations in ν' and ν''.

At very high fields we can readily see what occurs by expanding Eq. (11) assuming $\nu\ll2\Delta\nu_n$. This gives in the same notation as before, for the shifted position, $W'-W''$, of any Zeeman component measured from the center of the original no field doublet lines

$$W'-W''=\pm\tfrac{1}{2}[(\nu'-\nu'')k+(1-k^2)(\nu'^2-\nu''^2)/y+\cdots]. \tag{28}$$

Here of course the second term becomes small for large fields and the first gives shifts symmetrical around $M=0$ (i.e., $k=0$) and thus $W'-W''\approx0$ for the center of gravity of components of either doublet member. In other words the original doublet is replaced by a single central band of limiting width $(\nu'-\nu'')$ which is just the original doublet separation. For CN this would require fields above 40,000 gauss for the widest doublets. In the case of many bands of N_2^+, however, the spin doubling is so small that all doublet appearance, on several plates taken by the author has vanished at fields as low as 2000 or 3000 gauss. Similar results have been reported by Fortrat.[35] Parker[36] states that his results are in harmony with Hill's equation but gives no details (except of course near perturbations where entirely different factors are predominant).

No $^3\Sigma\rightarrow{}^3\Sigma$ bands have been observed in the field though presumably a second order con-

[35] Fortrat, Ann. de Physique **3**, 345 (1915); also reference 26.

[36] Parker, Phys. Rev. **44**, 87 (1933).

traction analogous to the above would take place.

In certain $^2\Sigma$ states involving a $d\sigma$ or $p\sigma$ electron unusually large spin doublings may develop due to an appreciable L_{perp} arising from L-uncoupling. This, as Watson and Bender[37] have shown, may lead to very large effects not accounted for by the simple theory outlined above. (See §10.)

7. Doublet States Intermediate Between Case (a) and Case (b) (Theory)

Since the great majority of molecular states are distorted by their own rotation, a state which may approximate fairly well at low rotation to case (a), becomes with high rotation more and more nearly case (b) and we therefore have all intermediate types of coupling in a given set of rotational states. Qualitatively then we should expect that a $^2\Pi$ state (intermediate between case (a) and case (b)) should for small J values and low enough fields give energy patterns determined by Eq. (9), which as the field increases (or J or both) should pass gradually into the Paschen-Back patterns to be predicted from Eq. (10). The precise way in which the transition occurs will of course depend on the value of $Y=A/B$ and of J and we should expect a large variety of effects in spectra otherwise rather similar.

Now Hill[38] has carried through a quantum mechanics calculation which applies to the whole range of intermediate cases, provided spin doubling in $^2\Sigma$ states and Λ-type doubling in all the rest be neglected. (The former have been treated separately above and the latter effects will be considered below.) He finds for the energy W of such a molecular state in a magnetic field (measured from the rotationless state)

$$W=\tfrac{1}{2}B[(\epsilon_1+\epsilon_2)\pm\{(\epsilon_1-\epsilon_2)^2+\delta^2\}^{\frac{1}{2}}] \tag{29}$$

where B is $h/8\pi^2cI$ and ϵ_1, ϵ_2 and δ are functions of K, J, Λ, Y, and the field H which may be abbreviated thus:

$$B\epsilon_1=f_1-\tfrac{1}{2}\tau_1, \quad (30) \qquad B\epsilon_2=f_2+\tfrac{1}{2}\tau_2, \quad (31)$$

$$\frac{B\delta}{2}=\Delta\nu_n\left\{\frac{(K+\frac{1}{2})^2M^2}{2\tau_1\tau_2\cdot(K+\frac{1}{2})^2}\right\}^{\frac{1}{2}}\left[(\tau_1+\omega_1)^{\frac{1}{2}}(\tau_2+\omega_2)^{\frac{1}{2}}\left\{1-\frac{\Lambda^2}{2K(K+1)}\right\}\right.$$

$$\left.+(\tau_1+\omega_1)^{\frac{1}{2}}(\tau_2-\omega_2)^{\frac{1}{2}}\left\{\frac{(K^2-\Lambda^2)\Lambda^2}{4K^2}\right\}^{\frac{1}{2}}-(\tau_1-\omega_1)^{\frac{1}{2}}(\tau_2+\omega_2)^{\frac{1}{2}}\left\{\frac{\Lambda^2[(K+1)^2-\Lambda^2]}{4(K+1)^2}\right\}^{\frac{1}{2}}\right]. \tag{32}$$

Here f, τ and ω, in turn, are abbreviations for functions of J, Y, Λ and H given by[39]

$$f(J,M)=B\{(J+\tfrac{1}{2})^2-\Lambda^2+\beta(\Lambda^2+\tfrac{1}{2})\}, \tag{33}$$

$$\tau(J,M)=B\{(2J+1)^2(1-\beta)^2+\Lambda^2(Y+\beta)(Y-4+5\beta)\}^{\frac{1}{2}}, \tag{34}$$

$$\omega(J,M)=B\{(2J+1)(1-\beta)-\Lambda^2(Y+\beta)/(J+\tfrac{1}{2})\}, \tag{35}$$

and

$$\beta=\Delta\nu_nM/[B(J+1)J].$$

In all cases the subscript 1 refers to states for which $J=K+\frac{1}{2}$ and subscript 2 to those with $J=K-\frac{1}{2}$ (where in all states outside the range $Y=0$ to $+4$ the latter are energetically *above* the former). In Eq. (29) the $+$ sign is to be assigned to subscript 1 states and the $-$ sign to subscript 2 states whenever $\epsilon_1>\epsilon_2$. When $\epsilon_2>\epsilon_1$ the reverse correlation is necessary, when the term under the radical must be written $(\epsilon_2-\epsilon_1)^2$ to insure the proper result when $\delta\to0$.

In the first place it is to be noted that Eq. (29) is considerably simplified for $J=K+\frac{1}{2}$ states when $M=\pm(K+\frac{1}{2})$ by the fact that δ as given by Eq. (32) vanishes and thus Eq. (29) reduces to

$$W=f[K+\tfrac{1}{2},\ M=\pm(K+\tfrac{1}{2})]-\tfrac{1}{2}\tau[K+\tfrac{1}{2},\ M=\pm(K+\tfrac{1}{2})],$$

[37] Watson and Bender, Phys. Rev. **35**, 1513 (1930).

[38] Hill, Phys. Rev. **34**, 1507 (1929).

[39] In Hill's Eq. (16) the factor B must be supplied.

which enables the overall width of Zeeman levels to be estimated with less labor for these spin states.

In the second place, for the lowest levels in $^2\Pi$, $^2\Delta$, etc., states $K=\Lambda$, $J=\Lambda-\frac{1}{2}$ and as Hill has shown (to the approximation to which δ is negligible) the energy determinant involved reduces to one term and this does not contain the field. Hence such states are magnetically dead in harmony with the inference made earlier (see Table I). For the exact description of course Eq. (29) must be used and a small magnetic effect is predicted which is very small when the spin doubling is large.

It can further be seen that for $^2\Sigma$ states, where $\Lambda=0$ and $\tau(J, M)=\omega(J, M)$, that Eq. (32) reduces to

$$\delta=(2\Delta\nu_n/B)\{[(K+\tfrac{1}{2})^2-M^2]/(K+\tfrac{1}{2})^2\}^{\frac{1}{2}}$$

and the two values of ϵ are, setting $J=K\pm\frac{1}{2}$,

$$\epsilon_1=[K(K+1)+\Delta\nu_n M/B(K+\tfrac{1}{2})] \quad \text{and} \quad \epsilon_2=[K(K+1)-\Delta\nu_n M/B(K+\tfrac{1}{2})]$$

when Eq. (29) reduces to $W=BK(K+1)\pm\Delta\nu_n$, which of course is simply the complete spin Paschen-Back effect giving the two sharp levels $2\Delta\nu_n$ apart predicted from Eq. (10) with $\Lambda=0$. (This result is to be expected since spin interaction for $^2\Sigma$ states was neglected in the deduction of Eq. (29).)

Now examination of the complete Eq. (29) shows that for a rather large range of $Y=A/B$ values $\delta\ll|\epsilon_1-\epsilon_2|$ and consequently that we may expand this equation in the form[39a]

$$W=\tfrac{1}{2}B\{(\epsilon_1+\epsilon_2)\pm(\epsilon_1-\epsilon_2)[1+\tfrac{1}{2}\delta^2/(\epsilon_1-\epsilon_2)^2-\tfrac{1}{8}\delta^4/(\epsilon_1-\epsilon_2)^4+\cdots]\};$$

assuming $\epsilon_1>\epsilon_2$ we have for the $J=K+\frac{1}{2}$ state,

$$W_1=B\epsilon_1+B\delta^2/4(\epsilon_1-\epsilon_2)-B\delta^4/16(\epsilon_1-\epsilon_2)^3+\cdots \tag{36}$$

and for the $J=K-\frac{1}{2}$ state

$$W_2=B\epsilon_2-B\delta^2/4(\epsilon_1-\epsilon_2)+B\delta^4/16(\epsilon_1-\epsilon_2)^3\cdots. \tag{37}$$

Now since Eqs. (36) and (37) are themselves rather involved it is either necessary to compute the pattern components for each molecule under consideration—or to expand them further for large values of the parameter Y. For this purpose let us examine the expression for ϵ (using J's instead of K's) where

$$\epsilon=(J+\tfrac{1}{2})^2-\Lambda^2+\beta(\Lambda+\tfrac{1}{2})\pm\tfrac{1}{2}[4(J+\tfrac{1}{2})^2(1-\beta)^2+\Lambda^2(Y+\beta)(Y-4+5\beta)]^{\frac{1}{2}}. \tag{38}$$

The radical term after some rearranging can be written:

$$\pm\tfrac{1}{2}Y\Lambda[1+2(3\beta-2)Y^{-1}]^{\frac{1}{2}}\left\{1+\frac{4(J+\frac{1}{2})^2(1-\beta)^2+\Lambda\beta(5\beta-4)}{Y\Lambda^2[1+2(3\beta-2)Y^{-1}]}\right\}^{\frac{1}{2}}, \tag{39}$$

where as the field increases from zero the fraction in the first radical is of the order of Y^{-1} and that under the second $J^2/Y^2(\Lambda=1$ or $2)$. Hence for $Y\gg J$ we should expect the first radical to be predominant, and to be able to write approximately for the displacement from the midpoint of the no field doublet (using Eq. (38) in Eqs. (36) and (37) combined, with subscript dropped and $\delta=0$)

$$W-B[J(J+1)-(\Lambda\pm\tfrac{1}{2})^2+\tfrac{1}{2}]=\pm B\left[\tfrac{1}{2}Y+\frac{(J+\frac{1}{2})^2-\Lambda^2}{Y\Lambda^2}+\cdots\right]\Lambda+(\Lambda\pm1)(\Lambda\pm\tfrac{1}{2})\beta$$
$$\mp\left\{2\left[\frac{(J+\frac{1}{2})^2-\Lambda^2}{Y\Lambda}+\cdots\right]\beta+\left[\frac{(J+\frac{1}{2})^2-\Lambda^2}{Y\Lambda}+\cdots\right]\beta^2+\cdots,\right\} \tag{40}$$

[39a] The actual range depends of course on the values of J used but in practice covers pretty well all but two (MgH and CH) of the $^2\Pi$ states which have been studied in the field. See Fig. 5 in this connection.

where all terms involving Y^{-1} to a higher power than the first are not retained. Here the terms not involving the field are—to the approximation used—simply the expansion for the rotational distortion of spin doublets as given by Hill and Van Vleck.[40] Eq. (40) while not as accurate for large J values as the expansion given by Hill (reference 38 Eq. (12′)) is more suited for the deduction of qualitative results. For we see as case (a) is approached the first power terms in β approach asymptotically as $Y\rightarrow\infty$ the result contained in Eq. (9) for a case (a) rigid molecule ($\Omega=\frac{1}{2}, \frac{3}{2}$). Also the first and second order fractional departures from Eq. (9) are respectively of the order of $\Delta\nu_n J/Y$ and $\Delta\nu_n^2/Y$ for the maximum values of M (the worst cases). Thus for $J=\frac{3}{2}$ and a $^2\Pi_{3/2}$ state we see that these contribute roughly fractions $8/3Y$ and $Z/3Y$, respectively (where Z is the field in tens of thousands of gauss), to the Zeeman shifts of Eq. (9). At $H=30{,}000$ gauss their contributions for all of the states in Fig. 5 with $|Y|$ values above that of ZnH is less than 4 percent. As J increases of course these eventually become dominant. On the other hand it is just these terms which prevent $^2\Pi_{1/2}$ states from being completely insensitive (see Table I) to the magnetic field for all J values (as they are of course for $J=\frac{1}{2}$ if $\delta\approx 0$). It should be noted further that each of these terms is of opposite sign to that of the spin displacement[41] $\pm Y/2$. Hence for low fields we expect magnetic levels with $M>0$ to be displaced slightly *inward* and those with $M<0$ slightly *outward* from their positions for pure case (a). At higher fields on the contrary *all* sublevels are displaced *inwards* towards the center of the doublet-levels due to the effect of the β^2 term (since $\beta^2\propto M^2$). The fictitious $M=0$ level remains to this approximation unaffected.

The expression for δ can unfortunately not be very readily simplified though it is small when Y is large and most significant for $|M|$ near zero. Fortunately also the last two terms in the long bracket of Eq. (32) are usually of about the same order of magnitude and practically cancel.

§8. Application of Hill's Theory to Typical Doublet Bands

In order to show the most interesting features to be expected Figs. 6, 7 and 8, give the calculated overall width of sublevels for several characteristic $^2\Pi$ states (calculated from Eq. (29) or the equivalent) and $^2\Sigma$ states (from Eqs. (11) and (12)). Fig. 6 is drawn for the $^2\Pi\rightarrow{}^2\Pi$ NO-β bands ($Y'=29$, $Y''=73$, $\epsilon_2>\epsilon_1$ for both levels). Fig. 7 is for the $^2\Sigma\rightarrow{}^2\Pi$ OH bands ($\gamma'=0.22$, $Y''=-7.47$, lower state inverted), and Fig. 8 for the $^2\Pi\rightarrow{}^2\Sigma$ MgH bands ($Y'=+5.7$, near case (b); γ'' not determinable from band due to extreme faintness of necessary satellites, but certainly small).

In the case of both $^2\Pi$ states of NO, Y is sufficiently large for the terms in δ^2 and higher in Eqs. (36) and (37) to contribute no more than 0.02 or 0.03 cm^{-1} to the total at 20,000 gauss. Since these terms are chiefly responsible for rendering the distribution of sublevels unsymmetrical about $M=0$, the curves are quite symmetrical as drawn. Since for low J values we are near enough case (a), for the $J=K-\frac{1}{2}$ states ($\mathbf{S}^*$ and $\mathbf{\Lambda}$ tending towards parallelism) the magnetic states with $M>0$ are *above* and these with $M<0$ are below the $M=0$ line. The exact reverse is true for large J (and K) values since now we are nearer normal case (b), where $\mathbf{S}^*$ tends towards antiparallelism with $\mathbf{K}^*$ and therefore makes positive contributions to the magnetic energy only when M is negative, and *vice versa*.

At the point where the curves cross the axis the average projection of the magnetic moment of $\mathbf{\Lambda}$ on $\mathbf{K}^*$ is positive while that of $\mathbf{S}^*$, which is on its way towards antiparallelism with $\mathbf{K}^*$, is negative and of the same magnitude. Hence the system as a whole is magnetically insensitive. The lower states ($J=K+\frac{1}{2}$) are to be regarded as almost essentially case (b) from near the beginning. The crossing overpoint (exact cancellation of effect of $\mathbf{\Lambda}$ and $\mathbf{S}^*$) now is shifted to the origin (formally at least $K=1$).

[40] Hill and Van Vleck, Phys. Rev. **32**, 262 (1928).

[41] It is necessary to bear in mind that the + and − signs of Eq. (38) do not correspond to the upper and lower members of the *same* spin doublet (same K value). Thus if K_1 and K_2 are neighboring values with $K_1+1=K_2=K$, say, the + sign goes with the upper (energetically higher) member of the $K_1=K+1$ spin doublet, for which $J=K_1-\frac{1}{2}=K+\frac{1}{2}$, while the − sign goes with that member (the energetically lower) of the doublet with $K_2=K$ which has the same *numerical* value of J, i.e., $J=K_2+\frac{1}{2}=K+\frac{1}{2}$.

Similar considerations hold for the $^2\Pi$ state of OH, Fig. 7, where however, the state is inverted case (a), which places the $^2\Pi_{1/2}$ state (which is insensitive at the origin) above the $^2\Pi_{3/2}$ state. Since in inverted states the $^2\Pi_{1/2}$ case (a) coupling passes into case (b) coupling with $J=K-\frac{1}{2}$ at large K values (reference 40 same page), the states with $M<0$ should lie above those with $M>0$. For the $^3\Pi_{3/2}$ state the magnetic energy splitting decreases in a perfectly regular way since now $\mathbf{\Lambda}$ and $\mathbf{S}^*$ parallel passes into $\mathbf{K}^*$ and $\mathbf{S}^*$ parallel without any anomalous crossing over. The limiting curves for high K approach the constant separation $2\Delta\nu_n$ since $\mathbf{\Lambda}$ is then nearly $\perp$ to $\mathbf{K}^*$ and its contribution averages zero over a revolution of the nuclei.

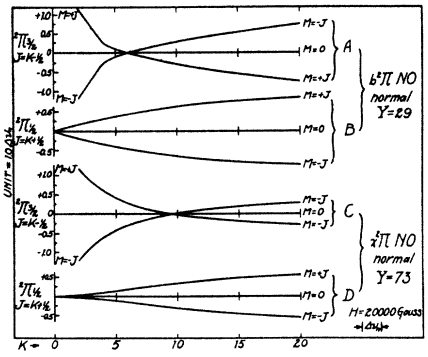

FIG. 6. Magnetic levels of the $^2\Pi$ states of NO (20,000 gauss). The extreme sublevels $M=\pm J$ and $M=0$ are plotted from Hill's equation in the form of Eqs. (36) and (37). The electronic level separations are not to scale. Due to the fact that δ is practically negligible the curves are symmetrical, the peculiar crossing over of the extreme levels in A and C being due to the correlation of quantum numbers as we pass from normal case (a) to normal case (b). Thus in A (or C) Λ and S are || near the origin (case (a)) but as K increases and the molecule passes into case (b) coupling, the state of Λ and S || goes into that of K and S *anti*-parallel. In the field therefore $M=+J$ has greater energy than $M=-J$ near the origin, but as the spin tends towards antiparallelism with K a point is reached where the time averages of Λ and S on K cancel precisely. Beyond this point $M=-J$ corresponds to S in the direction of the field and therefore lies above $M=+J$. In B (or D) in contrast Λ and S are antiparallel for $K=0$ and hence cancel in their magnetic effect at this point. As then S gradually breaks away from its coupling to the axis towards parallelism with K, the states with $M=+J=K+S$ remain above those with $M=-J$. The crossing over in C occurs later than in A because the coupling constant and hence Y is greater in the lower state. In the $^2\Pi$ state of ZnH ($Y=46.7$) the crossing occurs at about $K=7$ and in CdH ($Y=167$) the curves do not cross but gradually approach one another, touching at around $K=17$.

In the case of MgH (Fig. 8) the spin doubling is so small (≈ 2 or 3 cm^{-1} near the origin, decreasing with K) that the complete Eq. (29) must be used since the contributions of δ are important. Due to the fact that δ contains the factor $(K+\frac{1}{2})^2-M^2$, it vanishes for $M=K+\frac{1}{2}$ and has its largest value for $M=0$. For this reason it is chiefly responsible for the asymmetry of the fictitious $M=0$ level, which divides the $(2J+1)$ sublevels so that as many lie above it as below it. It therefore aids in determining roughly, in the absence of intensity calculations which would be rather involved, where the maximum intensity in a given block of unresolved components should fall. Since further for the $J=K-\frac{1}{2}$ levels (the higher members) the plus sign in Eq. (29) is used while for the lower, $J=K-\frac{1}{2}$ levels, the minus is used, the presence of an appreciable δ causes the two $M=0$ curves to be

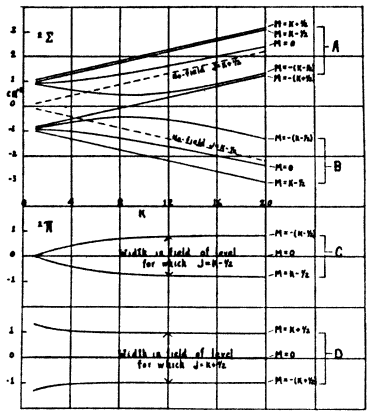

FIG. 7. Magnetic levels of the $^2\Sigma$ and $^2\Pi$ states of OH (20,000 gauss). The sublevels of the $^2\Sigma$ levels ($\gamma=0.22$) $(K+\frac{1}{2})$ are drawn from Eq. (11) and those of the $^2\Pi$ state ($Y=-7.47$) from Eq. (29) (after Almy, reference 46). The sublevels are divided in each case into equal groups by the fictitious $M=0$ level. The marked crowding of sublevels *above* the zero field position (dotted line) in A and *below* it in B should be noted since it is precisely this effect (more marked for smaller spin doubling) which underlies the contraction of $^2\Sigma\rightarrow{}^2\Sigma$ lines in the field (cf. N_2^+ and CN). Since here $Y=-7.47$ the $^2\Pi$ state is *inverted* and the condition of Λ and S || at the origin passes with increasing K into that of K and S || and no crossing over occurs (D). In the $J=K-\frac{1}{2}$ states, however, Λ and S antiparallel passes into K and S antiparallel and consequently the states with $M=-J=K-\frac{1}{2}$ lie above those with $M=+J$ (C). It is a striking fact that with such a small value of Y, only 7.47 units from the nearest pure case (b) value, we have practically complete symmetry of the sublevels around the $M=0$ curves.

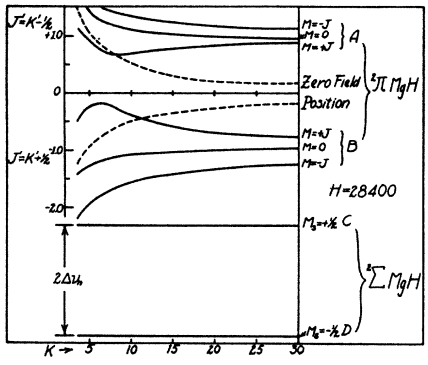

FIG. 8. Magnetic levels of the $^2\Pi$ and $^2\Sigma$ states of MgH (28,400 gauss). Due to the extreme faintness of the necessary satellites in the MgH bands the value of γ in the $^2\Sigma$ cannot be found. Accordingly the curves for this state are drawn assuming a complete Paschen-Back effect for all K values (C and D). Since $Y=+5.7$ we are so near the case (b) interval of 0 to $+4$ that the complete Eq. (29) must be used for the $^2\Pi$ state. The results are shown in A and B where the dotted curves are the theoretical separations of the zero field levels as computed from Hill's and Van Vleck's doublet expression. (This considerably underestimates the separation for large values of K.) The practical attainment of the Paschen-Back conditions for the largest K values is indicated by (1) the approach of the $M=0$ curves to a separation of very nearly $2\Delta\nu_n$ and (2) the near attainment of the zero-field doublet separation as the actual overall spread of the sublevels in groups A and B.

pushed apart symmetrically about the doublet centers. The dotted lines represent the no field doublet intervals as calculated from Hill and Van Vleck's Eq. (27)[40] and therefore does not include Λ-type doubling. It thus does not differentiate between P, Q and R doublets.

§9. Experimental Results for Doublet Type Bands

MgH ($^2\Pi\rightarrow{}^2\Sigma$) and OH ($^2\Sigma\rightarrow{}^2\Pi$)

In Figs. 9 and 10 are given a few of the typical Zeeman patterns to be expected in MgH and OH. The Zeeman effects in the MgH bands have been studied qualitatively by Watson and Parker[42] and quantitatively in some detail by Almy and the author[43] at a series of field strengths from around 5000 to 28,400 gauss. The complete patterns of the lines with $K'=1$ were successfully resolved at the highest fields as was the 6 component part of the $P_1(3\frac{1}{2})$, $(K'=2)$ pattern—the negative half appearing as a confused faint band with individual lines too indistinct to measure. The observed and measured patterns are shown in Fig. 9 for comparison. For intermediate K values the *high* frequency member of a doublet (P_2, Q_2, R_2 lines) splits into diffuse doublet-like patterns of separation roughly $2\Delta\nu_n$—while the *low* frequency members (P_1, Q_1, R_1 lines) give unresolved bands of about the same width. As the field is increased for a given K (or K for a given field) the members of a doublet must be considered as a whole since now the inner blocks broaden, move in and eventually overlap, filling the no field doublet interval with a broad, diffuse, though quite intense band. The outer components or wings on the other hand move farther out, become very faint indeed and approach a total separation of practically $4\Delta\nu_n$. The lower part of the figure shows this behavior for two typical cases ($K'=5$ and 28). The general agreement with the predictions is quite satis-

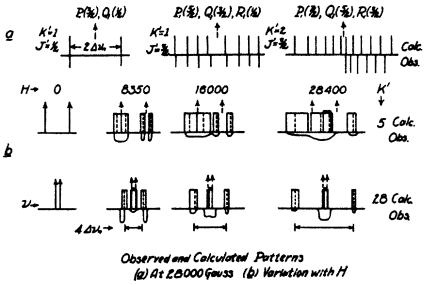

FIG. 9. Predicted and observed patterns of MgH. (a) In the upper part of the diagram are represented the predicted patterns for some of the early lines (drawn upward) and (drawn downward) the observed positions of components where they were resolved. ($H=28{,}400$ gauss.) Intensities are not represented. In the case of the $K'=2$, $J'=3/2$ patterns the appearance of the patterns is about that predicted though the scale is too small. (b) Here are shown the calculated and observed (sketched only qualitatively) patterns for $K'=5$ and $K'=28$ as the field varies from a low value to a field giving a nearly complete Paschen-Back effect even for the $K'=5$ doublets. Here the dotted lines represent the fictitious transition $M'=0\rightarrow M''=0$ and hence in a general way suggest where the most intense part of a pattern should lie. The most serious discrepancy is the too low width of the central part of the pattern as predicted—which is undoubtedly connected with the failure of the Hill and Van Vleck doublet formula to represent the no field doublet widths at high K values (it predicts only about a third of the observed value)—as well as with the complete neglect of spin doubling in the $^2\Sigma$ state.

[42] Watson and Parker, Phys. Rev. **30**, 592 (1927).
[43] Almy and Crawford, Phys. Rev. **34**, 1517 (1929).

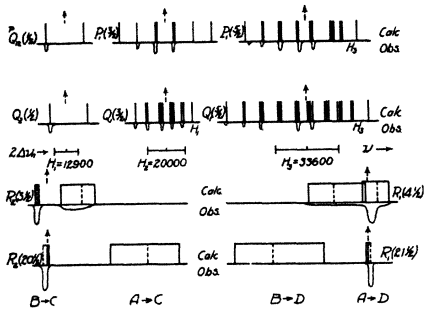

FIG. 10. Predicted and observed patterns in OH. The patterns not labelled H_1 or H_3 all refer to computations and observations at $H_2=20{,}000$ gauss. Here $H_1=12{,}900$ and $H_3=33{,}600$. The general quantitative agreement in the case of all patterns which could be measured is very good. The failure to observe the inner blocks in the case of the highest lines is perhaps not surprising when the extreme width over which the components are spread is considered. Here the designations $B\rightarrow C$, $A\rightarrow C$, etc., indicate transitions between the corresponding groups of levels in Fig. 7.

factory—the chief discrepancies being (1) the central band is slightly wider than calculated and (2) the wings are too narrow. Both of these discrepancies would be reduced by the presence of spin doubling in the $^2\Sigma$ state, which is presumably therefore the source of part at least of the disagreement.

In the case of OH, although the value of $|Y|$ (7.47) is still small it is over four times as far removed from the nearest case (b) value, O, as is MgH from $Y=+4$. This is sufficient to cause striking differences in the patterns obtained in the two cases. (See Fig. 10.) The earlier qualitative observations made on the band lines of OH by Deslandres and d'Azambuja[44] and Fortrat[45] agree well with the predictions of Hill's equation. Later Almy[46] with somewhat better experimental conditions studied in detail the behavior of the 13 observable branches and succeeded in resolving and measuring in whole or in part all of the low K-value patterns shown in Fig. 10, the measured displacements being in good quantitative agreement with predictions. For convenience the patterns resolved at 20,000 gauss are plotted *downward* and the theoretical ones upward. For the behavior at the higher K-values the R_1R_2 lines may be taken as typical. Here the inner blocks which overlapped and produced the most striking part of the MgH patterns, become wider and *fainter* as the field is increased but never overlap. In fact at the highest fields and K-values they are too faint to photograph. The outer components, the wings of MgH, are displaced *outward* only slightly and are almost as intense as the no field lines. Since this displacement decreases rapidly with K—the higher lines for short exposures show very little visible change in the field. The conditions then which are reached in MgH at 2000 or 3000 gauss are just being reached in OH at 30,000 gauss or more. Because of these striking intensity differences we see why multiplet lines for states near case (b) are usually reported as giving simply broad bands the width of the original doublets (the *wings* usually too faint to register) while higher multiplet lines nearer case (a) are reported as not appreciably affected (*inner* components too faint to register).[47]

ZnH, CdH and HgH ($^2\Pi\rightarrow{}^2\Sigma$)

The $^2\Pi\rightarrow{}^2\Sigma$ bands of ZnH ($Y'=46.7$: $\gamma''=0.223$) have been studied by Hulthén[48] and Watson and Parker[49] who reported that although the Q_1 and Q_2 and the earlier R_1 and R_2 lines gave doublet-like patterns in the field, the higher R lines and all of the P lines (above say $K=4$) seemed quite unaffected by the field. The Q_1 branch patterns could be measured as far as $K=13$ when they fused into a single band. Hulthén states that similar results were obtained by him in the HgH bands ($Y'=570$, $\gamma''=210$) though no details are given.

At first sight these results seem hard to reconcile with expectations particularly with the upper state so near case (a). More detailed examination by Watson[50] has, however, shown as we might expect from the results with MgH and OH that all apparent contradictions are removed when sufficiently prolonged exposures are made

[44] Deslandres and d'Azambuja, C. R. **157**, 814 (1913).
[45] Fortrat, J. de Physique **5**, 20 (1924).
[46] Almy, Phys. Rev. **35**, 1495 (1930).

[47] The extreme faintness of the wings is due to the attainment of an almost complete Paschen-Back effect in the $^2\Pi$ state of MgH with the selection rule $\Delta Ms=0$ being more and more nearly rigorous.
[48] Hulthén, Thesis, Lund (1923).
[49] Watson and Parker, Phys. Rev. **30**, 596 (1927).
[50] Watson, Phys. Rev. **36**, 1134 (1930).

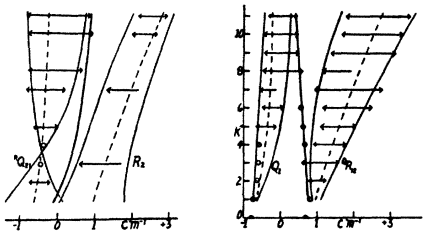

FIG. 11. Zeeman patterns of ZnH. (a) shows the computed overall widths of the patterns of the Q_1 and ${}^{Q}R_{12}$ lines of the ZnH band ($H=16{,}400$) after Watson (reference 49). The displacements are calculated from the zero field Q_1 line as origin, and the dotted curves represent the transitions $M'=0\rightarrow M''=0$. When the observed components are sharp lines their position is indicated by a circle —otherwise by a properly placed arrow. The peculiar drawing together caused by the crossover line between the two blocks results from the crossing over of the $M=-(K+\frac{1}{2})$ energy level in the ${}^2\Sigma$ patterns shown in Fig. 7 for OH. This is the cause of the rough doublet patterns contracting with K which have been reported for the Q lines of this and similar bands. (b) Zeeman patterns for the ${}^{R}Q_{21}+R_2$ lines. (The zero field ${}^{R}Q_{21}$ lines are taken as origin.) The sudden constriction of the width of the ${}^{R}Q_{21}$ block at $K''=4$ is particularly striking and the direct result of the crossing over of the extreme levels in the ${}^2\Pi$ state (see Fig. 6 where the curves are quite similar to those of ZnH).

to record the fainter parts of patterns. Fig. 11 show the predicted (solid curves) and observed (circles and arrows) patterns for the R_2 and Q_2 lines and their accompanying satellites. Quite similar results were found for the ${}^{0}P_{12}$ branch lines, the low frequency parts of the patterns being merely very faint.

Similar results were also obtained by Watson[50] for the analogous CdH bands [$Y'=167$, $\gamma''=0.592$], where now due to the large value of Y the curves representing the overall spread of Zeeman sublevels (cf. Fig. 6) for the ${}^2\Pi_{3/2}$ substate no longer cross the axis but converge slowly to a zero separation near $K=19$.

NO-γ ($a\,{}^2\Sigma\rightarrow x\,{}^2\Pi$) and NO-$\beta$ ($b\,{}^2\Pi\rightarrow x\,{}^2\Pi$) bands

In the NO-γ bands we have an appreciable spin doubling in the upper state and $Y=73$ for the lower state. We therefore expect results rather similar to those for ZnH modified slightly by the fact that the sublevel width curves (Fig. 6 lower half) now cross one another at a slightly higher K value, i.e., 10 instead of 6 or 7. Further the ${}^2\Pi$ state being nearer case (a) the satellite branches have more nearly the intensity of the main branches. Observations on these bands by Fortrat[51] and Pogany and Schmid[52] both indicate doublet-patterns in all lines studied, those in the Q_1 branch as in ZnH being most distinct and observable over the longest range. Their width decreased from about $2\Delta\nu_n$ near the origin to near $\Delta\nu_n$ at $K=32$. Fig. 12 shows[53] the magnetic levels and the patterns to be expected theoretically for members of a P, Q or R no field doublet with $K''=10$. Here the blocks of components for the high frequency line are somewhat broader and closer together than those for the low frequency line. The observed widths agree substantially with these to be expected from such a diagram. (Thus for $Q_1(10\frac{1}{2})$ the observed separation is 92 percent of the distance between the dotted lines ($M'=0\rightarrow M''=0$ transition) in the lower pattern of Fig. 12.) The peculiar observation recorded by Pogany and Schmid that they could measure *no* effect at all at 12,000 gauss whereas that at 17,000 was as great as that at 26,000 gauss is difficult to understand. If it should be confirmed on instruments of higher resolving power (particularly for the lines of low K values) it would be a definite contradiction to the theory.

In the NO-β bands we have a ${}^2\Pi\rightarrow x\,{}^2\Pi$ transition, the lower level being common to the β and γ bands. Here $Y'=28$ and $Y''=73$ so that the crossing of the energy curves in Fig. 6 occurs

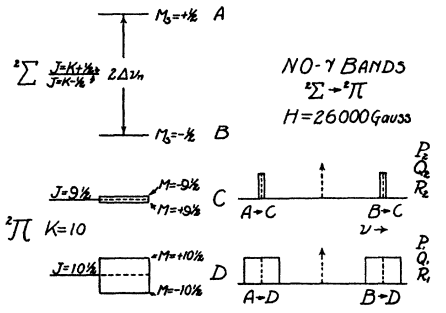

FIG. 12. Predicted patterns for $K''=10$ doublet of NO-γ bands.

[51] Fortrat, C. R. **156**, 991 (1913); Ann. de Physique **3**, 345 (1914).

[52] Pogany and Schmid, Zeits. f. Physik **49**, 162 (1928).

[53] Almy, Thesis, Harvard University (not published in extenso).

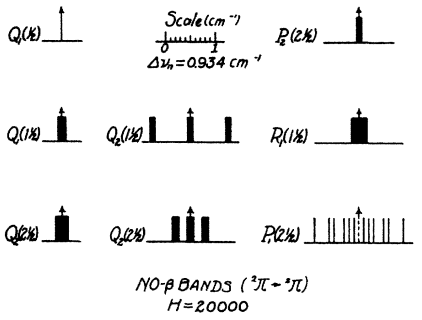

FIG. 13. Predicted patterns for early lines of NO-β bands. The arrows indicate zero field positions and are dotted when the central position is free of radiation. It is probable that only $Q_2(1\frac{1}{2})$ and $Q_2(2\frac{1}{2})$ could be resolved and then of course only into their gross structure. An examination of the magnetic energy curves of Fig. 6 shows that the higher lines should give nothing but broad bands —the width being roughly the same at high K values for all branches.

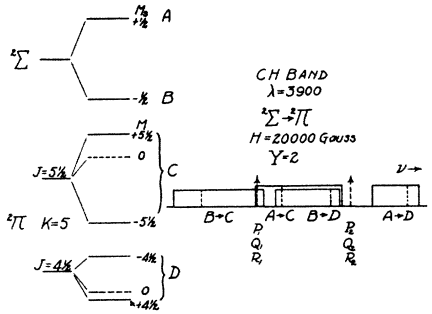

FIG. 14. Predicted patterns for $K''=5$ doublet of CH band ($\lambda=3900$).

sooner for the initial state. The curves for the $^2\Pi_{1/2}$ states are quite similar. As a result we should expect only a few of the early lines to give characteristic patterns, in particular $Q_2(1\frac{1}{2})$ and $Q_2(2\frac{1}{2})$. See Fig. 13 where the theoretical patterns are sketched for $H=20{,}000$ gauss.[54] All higher lines should give only broadened bands the total widths of which should for the P_1, Q_1, R_1 branches increase slowly with K. The P_2, Q_2, R_2 patterns should decrease at first to a minimum and then increase to about the same value. The total width of a high K pattern should not exceed 40 percent of $2\Delta\nu_n$. In this case the observations reported by Pogany and Schmid[55] are of an entirely different character. They report qualitatively that each line gives a doublet, the separation approaching $2\Delta\nu_n$ at the origin, which of course is the characteristic behavior of a $^2\Sigma\rightarrow{}^2\Pi$ and not of $^2\Pi\rightarrow{}^2\Pi$ transition. Yet there seems to be no doubt that the double headed red-degraded bands which they photographed at λ2488, 2428 and 2326 are $^2\Pi\rightarrow{}^2\Pi$ bands, and really belong to the β-system. It is evident that further observations at higher dispersion are very much to be desired since it is quite difficult to understand how such rigid $^2\Pi$ states could behave in this fashion.

[54] These calculations were kindly made by Professor G. M. Almy.

[55] Pogany and Schmid, Zeits. f. Physik **59**, 42 (1929).

CaH ($^2\Pi\rightarrow{}^2\Sigma$) band

In the $^2\Pi\rightarrow{}^2\Sigma$ CaH band at λ7000 we have $Y'=18.5$ and $\gamma''\approx 0.80$ (a very large value) and the Zeeman patterns for the *early* lines are quite well described by Hill's theory.[56] Several peculiarities, however, require comment. At or near $K=19$ in the $^2\Pi$ state the T_1' and T_2' levels which are normal for low J with $T_2'(J)>T_1'(J+1)$, approach and cross over with thereafter $T_1'>T_2'$. On the lower side therefore of this point we have pattern changes over a range of two or three units in K which in MgH were only observed over a range of 20 or 30 units. Furthermore as K increases the observed patterns show a steady and increasing departure from the predicted ones, which indicates a progressive uncoupling of L from the nuclear axis. This together with the analogous results for the λ6389 ($^2\Sigma\rightarrow{}^2\Sigma$) band will be considered in more detail in Section 10.

CH ($^2\Sigma\rightarrow{}^2\Pi$) band

In the case of the λ3900 band of CH we have a $^2\Sigma\rightarrow{}^2\Pi$ transition with $Y''=2$ and thus a state in the center of the case (b) range of Y-values. Hulthén[48] reports that the high frequency member (P_2, Q_2, R_2 lines) of each no field doublet is split into an asymmetric doublet by the field, the positive component being displaced more than the negative. The width of this doublet pattern varies linearly with H for low fields, being $2\Delta\nu_n$ near the origin and decreasing with K. Furthermore, the positive component becomes fainter with both increasing K and H

[56] Watson and Bender, Phys. Rev. **35**, 1513 (1930).

eventually disappearing all together. The lower frequency members (P_1, Q_1, R_1 lines) on the contrary were not doubled but displaced slightly inward. These facts together with the observation of Fortrat[57] on non-linearity with the field as soon as it was high enough to alter intensities, are quite reminiscent of the early lines of MgH. For purposes of comparison Fig. 14 shows the calculated energy levels and patterns[58] for doublets with $K=5$. As far as the data are recorded they seem to be in substantial agreement with theory, the importance of the δ term of Eq. (32) being in agreement with Fortrat's observation of the great importance of square terms (in H) at higher fields.

It thus appears that, with a few exceptions, the experimental observations over a large range of Y values intermediate between pure case (a) regular and pure case (a) inverted are in excellent agreement with the theoretical expressions deduced by Hill. Further it seems that the total width of unresolvable blacks of components when taken with the location of the important, though fictitious, $M'=0\rightarrow M''=0$ component is sufficient for an interpretation of most of the data without the necessity of detailed intensity calculations.

§10. Zeeman Effect in Singlet States with L-Uncoupling[58]

In the cases thus far considered it has been assumed that the energy of binding of the resultant $\mathbf{L}^*$ vector to the nuclear axis was very large or more precisely that A_L the separation, for example, of the Π and Σ states arising from a given p-electron was very large compared with the greatest $\Delta\nu_n$ resulting from attainable fields. When $\Delta\nu_n$ was of the same order of magnitude as A_S, the separation of spin multiplet components, we had spin uncoupling as a direct analogue of the Paschen-Back effect in atoms. Similarly here when $A_L \approx \Delta\nu_n$ we might have uncoupling of the $\mathbf{L}$ vector produced by the field, with a new sort of Paschen-Back effect having no analogue in single atoms. Actually A_L, is much too large[59] for this to be a significant effect at attainable fields, the $\mathbf{L}^*$-uncoupling being usually connected with the rotation of the nuclei and the resultant quantization of $\mathbf{L}^*$ not along the figure axis but along the direction of the *nuclear angular momentum* which is now itself quantized, taking on the value $[R(R+1)]^{\frac{1}{2}}$ (where R is integral).

Under these circumstances of course, Λ ceases to be a quantum number and the usual Σ, Π, Δ notation loses its significance. We may speak of the states resulting from a given L-value[60] as a p- or d-*complex* ($L=1$, 2) where the passage from the states of firm coupling to those of complete

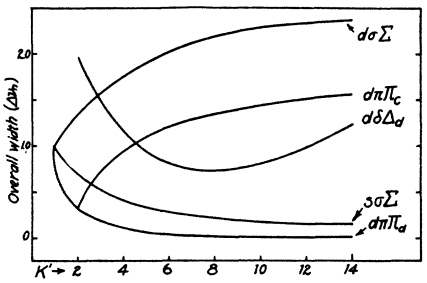

FIG. 15. Semi-qualitative magnitudes of Zeeman patterns of He_2 lines. These curves are similar to the qualitative curves given by Harvey modified by the later data obtained by Mills. They represent rough overall widths of patterns involving transitions from $d\sigma$, $d\pi$ and $d\delta$ states in which L-uncoupling is increasing with K to the $2p\pi\,{}^3\Pi$ state which is known to be case (b') very closely. The $s\sigma\,{}^3\Sigma$ curve represents a $s\sigma\,{}^3\Sigma\rightarrow 2p\pi\,{}^3\Pi$ transition which therefore gives just the same values as those obtained for $^1\Sigma\rightarrow\Pi$ bands in CO. The effect drops off very rapidly in the $d\pi\,{}^3\Pi_d\rightarrow 2p\pi\,{}^3\Pi$ lines due to the fact that L_{perp} is tending toward a zero value.

uncoupling may be correlated as follows. In pure case (a) coupling the $\mathbf{L}^*$ vector executes pure precession about the axis of figure and its component along the axis of nuclear rotation (or what is nearly the same thing along $\mathbf{K}^*$) averages to zero over electronic cycles. Further right- and left-handed rotations have identical energies (i.e., $+\Lambda$ and $-\Lambda$ are equivalent). As rotation, however, increases, this degeneracy[61] is removed and the interaction or resonance between $+$ and $-$ values of Λ causes a splitting into pairs of levels—

[57] Fortrat, Ann. de Physique **19**, 81 (1923).

[58] Similar considerations obtain in multiplet states when the spin multiplicity is of negligible magnitude.

[59] See in this connection Mulliken and Christy, Phys. Rev. **38**, 87 (1931).

[60] Actually of course such simple conditions are likely to occur only when we are dealing with a *single* p- or d-electron in an excited state, in which $L\equiv 1$. With this in mind the above use of L will lead to no misconceptions.

[61] Van Vleck, Phys. Rev. **33**, 467 (1929).

socalled Λ-doubling. We may say that the component of $\mathbf{L}^*$ ⊥ to the axis of figure instead of precessing steadily either speeds up or slows down when nearly parallel (or anti-parallel) to $\mathbf{K}^*$ with the result that a non-vanishing component of $\mathbf{L}^*\perp$ to the axis of figure, L_{perp}, develops. It is this non-uniformity of precession essentially, which removes the degeneracy in the sign of Λ and causes the Λ-type doubling. Now as the rotation increases we may eventually have the precession of $\mathbf{L}^*$ around the axis of figure entirely overcome, with Λ ceasing to exist, and L_{perp} tending to have quantized integral values along $\mathbf{R}^*$.

The values towards which L_{perp} tends depend upon the type of electron state we are considering. Thus for regular states (Δ state above Π, Π above Σ) we have a $d\sigma$ electron tending towards $L_{\text{perp}}=+2$, $d\pi_c$ and $d\pi_d$ electrons to $+1$ and 0 while $d\delta_c$ and $d\delta_d$ go towards -1 and -2. Similarly if $A_L>0$ (when the Π state is above the Σ state) we have $p\sigma$, $p\Pi_d$ and $p\Pi_c$ electrons tending respectively to $+1$, -1 and 0.[62]

We then have $\mathbf{R}^*$ and $\mathbf{L}^*$ precessing around their resultant $\mathbf{K}^*$, where for a given R, K takes on the values $(R+L)$, $(R+L-1)$, $\cdots(R-L)$. If now the coupling of $\mathbf{L}^*$ and $\mathbf{R}^*$ is sufficiently large we may expect (for low fields and large enough K at least) that the magnetic energy may be obtained by finding the time average of $\mathbf{L}^*$ along $\mathbf{K}^*$ and considering the $(2K+1)$ positions which the system can assume as M goes from $+K$ to $-K$. But the time average of $\mathbf{L}^*$ is simply its projection on $\mathbf{K}^*$ or $[K(K+1)+L(L+1)-R(R+1)]/2[K(K+1)]^{\frac{1}{2}}$ and hence we may write[63] Eq. (15).

$$W=M\frac{[K(K+1)+L(L+1)-R(R+1)]}{2K(K+1)}\Delta\nu_n. \quad (41)$$

Here due to the fact that the coefficient of $\Delta\nu_n$ in Eq. (41) may remain rather large even for the largest K values we are led to expect magnetic effects of a larger magnitude than any thus far discussed. Furthermore the effects for the various members of a p- or d-electron complex, including in a complex[63a] all the limiting uncoupled states resulting from a common type of excited electron, will differ in a characteristic manner. Thus in a d-complex the greatest spread of magnetic-sublevels will result from $d\sigma$ and $d\delta$ states while the least from $p\pi_c$ states. In a p-complex the $p\sigma$ and $p\pi_d$ for complete uncoupling give effects which are similar while of course s electron-states remain insensitive $(R=K,\ L=0)$ Weizel[64] has shown further that L-uncoupling in light molecules should increase with the total quantum number, n, of the excited electron, with K and with the difference, $(L-\Lambda)$ between L and its projection Λ on the axis of figure. Thus we should expect it to increase in a series $nd\delta\Delta$, $nd\pi\Pi$, $nd\sigma\Sigma$ and in a given configuration to be more marked for the highest states of excitation of the electron and for the greatest nuclear rotation.

In the case of H_2 where L-uncoupling in singlet states is very marked—although the observations are fragmentary and made with too little dispersion it can be said that the lines showing the most definite and largest effects are these involving $d\sigma\,{}^1\Sigma$ levels. Thus consider the $3d\sigma\,{}^1\Sigma\rightarrow 2p\sigma\,{}^1\Sigma$ lines. Here both states show evidence of uncoupling and should therefore be magnetically active at large K. For the upper state l_{perp} tends towards $+2$, $K=R+2$ and therefore $W=2M\Delta\nu_n/K$ from Eq. (41). Consequently the overall width of the group of magnetic levels is $4\Delta\nu_n$. For complete uncoupling l_{perp} for the lower state should tend towards $+1$ giving therefore a group of sublevels, $2\Delta\nu_n$ in width for all K-values. In other words transitions of this type should give bands (for all K-values) which are of the same overall width, $2\Delta\nu_n$. Further, observations longitudinal to the field should give patterns of the same overall intensity distribution (twice as intense in absolute magnitude) as for transverse observation and ⊥ polarization. As Mills has shown (see Fig. 16) all P and R lines in this polarization tend to be more

[62] See Mulliken, *Interpretation of Band Spectra*, Part I (see reference 1) Figs. 13 and 14, where the correlations for case b′ and case d′ for p- and d-electrons are given in detail. Here for Fig. 13 the a and b Λ-doubling substates are to be correlated with the later c, d nomenclature while for Fig. 14 the same thing holds for the substates of the d′Δ states but the reverse for the $d\pi$ states. See Mulliken's Review, Part IIc, footnote 57.

[63] J. S. Mills, Phys. Rev. **38**, 1163 (1931).

[63a] See Weizel, *Bandenspektren*, p. 120 *et seq.*

[64] Weizel, Zeits. f. Physik **54**, 321 (1929).

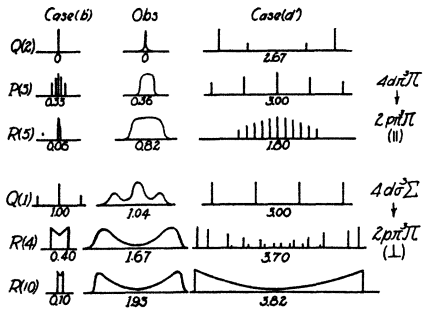

FIG. 16. Observed Zeeman patterns in He_2 lines. Here are represented a few of the more striking patterns obtained in the $4d\pi\ ^3\Pi \rightarrow 2p\pi\ ^3\Pi$ and $4d\sigma\ ^3\Sigma \rightarrow 2p\pi\ ^3\Pi$ bands of He_2 by Mills. On the left are shown the patterns expected for pure case (b') coupling and on the right these for complete uncoupling of $\mathbf{L}^*$ with the axis of figure (case (d')). (The number beneath each pattern is the total width in $\Delta\nu_n$.) In between are sketched roughly the patterns observed. The close agreement with the patterns on the left for the first lines and the great departure for the higher lines indicates clearly the progress of the uncoupling. (It is of course by no means complete in these bands.)

intense at the edges than at the center and hence should have a broad doublet appearance. This seems to be in agreement with some observations of Dufour[64a] on H_2 band-lines with longitudinal observation—when he finds that those which are sensitive (the majority are not) give just such rough doublets around $2\Delta\nu_n$ or below in width.[65] Other observations by Dufour[66] and Croze[67] in the Fulcher bands which are $p\pi\ ^3\Pi \rightarrow s\sigma\ ^3\Sigma$ bands, indicate no appreciable Zeeman effects. This must indicate then that since the lower state is insensitive the $p\pi\ ^3\Pi$ states exhibit no L-uncoupling. (The spin being so feebly coupled to the rest of the molecule, it is completely uncoupled at low fields and we are justified in treating these as singlet states.) It is of course conceivable that the coupling $I(\mathbf{R}^*, \mathbf{L}^*)$ may be sufficiently weak for the field to overcome it entirely in which case we should have transitions from 5 upper states, $M_L=0$, ±1 and ±2, to 3 lower ones with $M_L=0$, ±1 which for longitudinal observation would give ($\Delta M_L=\pm1$) a doublet of separation $2\Delta\nu_n$— the sharpness of the components of which would be determined by the residual coupling $I(\mathbf{R}^*, \mathbf{L}^*)$ in the two states. It is apparent that more observations at higher dispersion are much to be desired.

L-Uncoupling in He_2 bands

In the case of the bands of He_2 the Zeeman effect, as influenced by more or less pronounced L-uncoupling, has been studied qualitatively by Curtis and Jevons,[68] for bands resulting from transitions from a d-complex to the $2p\pi\ ^3\Pi$ state of ortho-helium and more extensively by Harvey[69] for a great many bands of similar types. Later Mills[70] has reported quantitative measurements together with comparisons of the predictions for case (b') [$I(\mathbf{L}^*, \mathbf{ax})$ large] and case (d') coupling [$I(\mathbf{L}^*, \mathbf{ax})$ negligible].

In harmony with the above considerations Harvey found that the $nd\sigma\ ^3\Sigma \rightarrow 2p\pi\ ^3\Pi$ bands[71] of He_2 show broad patterns of practically uniform width for all high values of K and further that as $n \rightarrow 4 \rightarrow 5 \rightarrow 6$ the size of the patterns definitely increases. For the $nd\pi\ ^3\Pi_c \rightarrow 2p\pi\ ^3\Pi$ bands the size of the pattern for a given n increases with K and for a given K with n. For $n=6$ they have become nearly as large as for those with $nd\sigma\ ^3\Sigma'$ as upper states. In both of these cases the effects are more marked for $\|$ polarization. For $nd\pi\ ^3\Pi_d \rightarrow 2p\pi\ ^3\Pi$ bands the effect is large at the origin (normal effect) and falls off rapidly with K. This is of course to be expected since for these upper states L_{perp} tends towards zero as case d' coupling is reached. In the case of $nd\delta\ ^3\Delta_d \rightarrow 2p\pi\ ^3\Pi$ bands the behavior is quite different. Here the patterns are large for low K values and decrease at first with K (normal behavior) only to increase again markedly as uncoupling sets in. Further the point of increase occurs sooner for

[64a] Dufour, Phys. Zeits. **10**, 124 (1900); C. R. **146**, 634 (1908).

[65] As Mills has pointed out the mere width of patterns, for low K-values is no indication of L-uncoupling, though such width for large K values is certainly a safe criterion. See reference 70, page 1154.

[66] Dufour, Ann. de Chem. et Physique **9**, 361 (1906), J. de Physique **8**, 258 (1909).

[67] Croze, Ann. de Physique **1**, 63 (1914).

[68] Curtis and Jevons, Nature **116**, 746 (1925); Proc. Roy. Soc. **A120**, 110 (1928).

[69] Harvey, Proc. Roy. Soc. **A126**, 583 (1929).

[70] Mills, Phys. Rev. **37**, 1005 (1931); **38**, 1148 (1931).

[71] The final state, $2p\pi\ ^3\Pi$, of these bands is known to be normal case (b') from the fact that other bands ending on it are of perfectly normal structure and intensity with practically negligible spin trebling.

$n=5$ than for $n=4$. Only one band of the type $d\delta\Pi_d \rightarrow 2p\pi\ ^3\Pi$ was observed ($n=4$) and the size of the patterns increased steadily with K. In Fig. 15 (after Harvey modified in the light of Mills' results), is shown qualitatively the characteristic behavior of the overall Zeeman patterns for these cases, where the $2p\pi\ ^3\Pi$ state is the common lower level (no uncoupling) and each curve is labelled with the initial state only. Precisely similar results of course obtain in para-helium ($S=0$) bands, for similar uncoupling.

Mills has observed a number of the ortho-helium bands and compared in detail the predictions for case (b′) coupling and complete Paschen-Back effect in both states, Eq. (10), with those when the initial state is assumed case (d′), Eq. (41), and finds that where the form of the bands suggests no uncoupling (such as in $3p\pi\ ^3\Pi \rightarrow 2s\sigma\ ^3\Sigma$ and $4d\delta\ ^3\Delta \rightarrow 2p\pi\ ^3\Pi$) the agreement with case (b′) predictions is in general good. On the other hand, for bands originating the nd-complex the patterns observed lie between the predictions of those two equations and are farther from these of case (b′) as n and K increase. A few of the more characteristic and striking patterns obtained by Mills are sketched in Fig. 16, where the intensities of the observed patterns are shown only roughly.

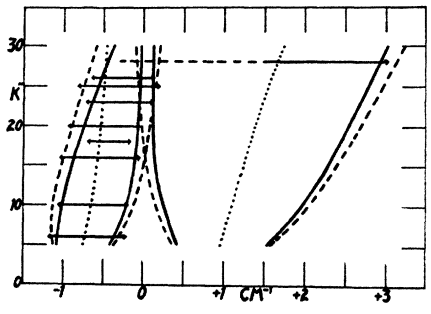

FIG. 17. Patterns of CaH R_1 lines. This figure (after Watson reference 72) shows the Zeeman patterns as calculated for the R_1 lines of the $^2\Pi \rightarrow ^2\Sigma$ bands of CaH from Hill's theory (full curves) and as modified by the effect of L-uncoupling (dashed curves). The dotted lines represent the $M'=0$, $M''=0$ transition. The effect of the L-uncoupling is thus seen to be sufficient to prevent these lines for high K values from exhibiting the characteristic doublet appearance expected for bands of the Y and K values involved. The effect is hardly observable for $K<5$.

L-Uncoupling in doublet states

As indicated above there was distinct evidence in the $4p\pi\ ^2\Pi \rightarrow ^2\Sigma$ and $4p\sigma\ ^2\Sigma \rightarrow ^2\Sigma$ bands of CaH of uncoupling in the upper states at high values of K. This led to progressive departure in the size of the observed patterns from those of Hill's theory. The fact that the spin doubling in the upper $^2\Sigma$ state is of the same magnitude as that of the $p\pi\Pi_d$ sublevels shows that these two levels are in the relation of pure precession or "pure precessional" mates.[62] Here for $K=33$, Δ_{12}, the spin doubling for the $^2\Sigma$ levels, is about 20 cm^{-1} and since $|\Delta_{12}|=A_S l_{\text{perp}}$ where A_S, the coupling constant of S with the axis, is -80, we have l_{perp} of the order of 0.25. Now Mulliken[62] has suggested that a reasonable approximation to the magnetic energy in such cases might be got by simply adding to the predictions of Hill's equations the proper projection of $l_{\text{perp}} \times \Delta\nu_n$. In this case since $A<0$, i.e., the $^2\Sigma$ state is above the $^2\Pi$, we have l_{perp} for the $p\sigma\ ^2\Sigma$ state tending towards -1. Consequently for the $J=K+\frac{1}{2}$ levels it *reduces* the total spread of the magnetic sublevels as given by Eq. (29) and increases it for the $K=K-\frac{1}{2}$ levels by the amount $2l_{\text{perp}} \times \Delta\nu_n$. The most striking effect of this for the $^2\Sigma \rightarrow ^2\Sigma$ bands is the *narrowing* of the broad components of the doublet-like patterns predicted by Eq. (11) for the R_1 lines and in causing these broad blocks to *overlap* near the no field position for the R_2 lines. This characteristic difference is precisely that found by Watson and his collaborators.[72]

In the $^2\Pi \rightarrow ^2\Sigma$ band the situation is more complicated. For lines originating in the $p\pi\ ^2\Pi_c$ levels—since here $l_{\text{perp}} \rightarrow 0$ as uncoupling proceeds—we expect to see no evidence of uncoupling. Hence the Q_1 and Q_2 branch lines should obey Hill's theory as these investigators find they do. On the contrary the P_1, P_2, R_1 and R_2 branch lines originating in the $p\pi\ ^2\Pi_d$ levels should show distinct discrepancies. Since the $^2\Pi$ state is normal (for low rotation at least) $^2\Pi_{1/2}$ is below $^3\Pi_{3/2}$. Also $^2\Pi_{1/2}$ case (a) is correlated with $J=K+\frac{1}{2}$ for case (b) and consequently the $p\pi\ ^2\Pi_d$ states with l_{perp} positive should lie *above* the $p\pi_c$ states for the F_1 levels

[72] Watson, Phys. Rev. **39**, 278 (1932). Cunningham, ibid. **41**, 389 (1932); Cunningham and Watson, ibid. **44**, 815 (1933).

and *below* the $p\pi_c$ states for the F_2 levels. These authors using the calculated l_{perp} for each line have added the corresponding contribution to the shifts predicted by Eq. (29). The effect is now to broaden the R_1 patterns until they overlap and to sharpen similarly the R_2 patterns. Fig. 17 shows the width of the R_1 lines as calculated from Hill's theory (full lines), the widths as corrected for uncoupling (dashed lines) and the observed broad bands (arrows). The results in this branch (as well as in the others) are in close agreement with observations.

§11. The Zeeman Effect Near Perturbations

Since the early work of Fortrat it has been recognized that near perturbations band lines show abnormally large sensitivity to the magnetic field. The effects may be classified as of two principal sorts (1) abnormally large patterns (for the K-value involved) often of the order of several Zeeman units and usually quite unsymmetrical in the intensity and displacement of components and (2) pronounced regularizing of irregular doublets and triplets at often rather small fields. The first type of effect may appear as a doublet or triplet of abnormally large size, when the normal doubling or trebling at that point in the multiple branch would be small or even unmeasurable.[73] In the majority of cases, however, a broad band unsymmetrical in intensity, the nature of which changes rapidly from line to line—is observed. The second type of effect observed by Bachem[33] and Fortrat and others can be most readily described by saying that the "sensitivity," as used earlier, of a doublet or triplet in the field $n\delta n/H^2$ possess abnormally large values for multiplets which are noticeably irregular. The effect of the field in a great majority of cases is simply to regularize the multiplet—which for higher fields then draws in as the neighboring regular ones.

The reasons for such behavior must be interpreted in the light of the discussions of perturbations in band spectra which have been given by Kronig[74] and Ittmann.[75] These indicate that whenever two energy levels of a molecule are close together and satisfy certain requirements, they will in general be pushed apart, the magnitude of the effect being determined by the strength of the resonance and the closeness of approach of the unperturbed levels. The conditions to be met are that the states involved shall (1) possess the same symmetry characteristics; (2) have Λ values differing by 0 or ± 1; (3) be of the same multiplicity; (4) have nuclear separations of the same order of magnitude; (5) have the same value of J and; (6) in the field have the same M-values. Of these it is probable that the 3rd conditions need not be considered in light molecules when intercombination transitions are known to exist. Now unfortunately any detailed discussion of how the magnetic levels of a given perturbed rotational state will behave requires quantitative information about the exact location of the perturbing level (or better where they would be without the perturbation)—and in the majority of cases at least, this is lacking since the very existence of the perturbing level as well as its approximate location must be inferred from a study of the perturbation itself. Further when the perturbation is a large one, even the slight energy shifts introduced by small fields should be sufficient to alter the interactions between magnetic substates so violently as to produce large Zeeman effects. This seems to agree with the general observations of Watson,[76] who studied in particular the perturbations in the (00) Angstrom band of CO and Parker who worked on the perturbations[73] of N_2^+, that the lines showing the greatest displacement due to the perturbation are the most sensitive to the field. The dependence of the effects on the exact locations of the interacting levels is also responsible for the great irregularity and in fact almost uniqueness of each pattern. Further than this one may not go in the way of general remarks though the following statements of qualitative features to be expected in certain cases may be made. For convenience the

[73] See for example Fortrat, reference 51 where an abnormally wide triplet is observed in a Swan ($^3\Pi \to {}^3\Pi$) band and Parker, Phys. Rev. **44**, 84 (1933), where wide doublets are observed near perturbations in the otherwise very narrow N_2^+ doublets. Similar large irregular patterns were observed by the writer in many lines of CO (reference 13).

[74] Kronig, Zeits. f. Physik **50**, 347 (1928).

[75] Ittmann, Zeits. f. Physik **71**, 616 (1931).

[76] Watson, Phys. Rev. **41**, 378 (1932); Phys. Rev. **42**, 509 (1932).

perturbed level will be referred to as level 1 and the perturbing as level 2. Levels of the same Ω, same Λ and same *size* of multiplicity (i.e., same coupling coefficients A_S) should show no appreciable disturbance in the field. This should be true not only for $^1\Sigma$ states which are rigid and hence have no splitting in the field but for those with $\Lambda \neq 0$. For under these conditions the sizes of the energy patterns in each level are the same and hence the field does not alter the *separation* of levels of the same M, whether level 2 is above or below level 1. Similar results should hold for say a $^1\Pi$ and a $^3\Pi_1$ state.[77]

If $(A_S)_1 \approx -(A_S)_2$ sensitivity to the field is to be expected. Since here if 1 is above 2 the levels of $+M$ are *separated* by the field and hence should suffer *less* perturbation while those of $-M$ are brought closer and would be more perturbed. The $M=0$ levels should not be much influenced unless we are near case (b) coupling. A bewildering variety of patterns could be obtained by simply varying the relative magnitudes of the essential factors, A_S, H, energy separation $W_1 - W_2$ of the two levels and $I(1, 2)$ the coupling or interaction energy of 1 and 2.

In particular we may expect that in some cases the actual order of the sublevels may be inverted and the overall width increased with the consequent production of a broad band in the field where otherwise (for the J value involved) a narrow line would be expected.

Similarly if state 1 is a doublet case (b) type while 2 is a doublet case (a) state—for large K values the latter would give only a narrow band of sublevels—while the first would give two groups several Zeeman units apart. An increasing field, if 1 and 2 were nearly coincident without perturbation, should therefore separate perturbing sublevels and eventually *reduce* the perturbation. Hence transitions to a lower state showing nearly complete Paschen-Back effect would result in a *regularizing* of the line by the field.

Finally, if either Ω or Λ or both are allowed to be different we shall have the greatest differences in pattern widths in the two cases and consequently, other conditions the same, the greatest disturbances and distortions of sublevel arrangement produced by the field. Since in such cases level 1 and level 2 take on properties intermediate and characteristic of both at and near a perturbation we may expect energy patterns which are more or less distorted averages of those for the normal unperturbed levels.

It is apparent from the above that the perturbations from which most quantitative information can be expected from Zeeman observations are these involving fairly well-known levels. It is further quite desirable that the actual perturbations shall not be too large—since then the very sensitivity to the field obscures the details of what is taking place.

[77] See Watson reference 76 where the behavior of several lines in CO seems to be of this nature. Here the expressions given for the splitting of the $^3\Pi_0$ and $^3\Pi_1$ states in the field are not correct—since the $^3\Pi_0$ state for case (a) as we have seen, Eq. (9), is *insensitive* due to the averaging to zero of the magnetic moment by the rotation. Likewise the splitting in the $^3\Pi_2$ state is 6 rather than 3 times $M\Delta\nu_n/[J(J+1)]$. This does not appreciably alter the qualitative aspects of his discussion.