# ZEEMAN EFFECT IN THE BAND SPECTRA OF AgH, AlH, ZnH, AND MgH

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Abstract

**Silver hydride bands.** The AgH bands were photographed in the second order of a 21-foot Rowland grating using field strengths of 10,000, 13,000, and 33,000 gauss. They exhibit no Zeeman effect whatsoever. This is a verification of the assignment $^1S \rightarrow {}^1S$ to this type of band.

**Aluminum hydride bands.** The observed broadening of the first lines in each branch is shown to agree quantitatively with the predictions of Van Vleck's formula for the change in energy produced by a magnetic field, providing the electronic transition is $^1P \rightarrow {}^1S$ and the values of $j$ given by the new mechanics are used. In agreement with the theory, all but the first lines in each branch show no effect.

**Zinc hydride bands.** The wide doublets (separation $= 2 \cdot \Delta\nu_{\text{norm}}$) found by Hulthén for the Q and R lines are shown to be quartets. These doublet separations tend to decrease at the highest field strengths. The $P_1$ and $P_2$ lines are unaffected at all field strengths up to 34,000 gauss. Hund's predicted first order Zeeman effect for his case b does not appear; that is, at field strengths strong enough to give a measurable effect the internal coupling of the spin axis is already broken down.

**Magnesium hydride bands.** At 10,000 gauss all the lines show a broadening, the spread of the pattern of the $P_1(5)$ line being 1.56 $\text{cm}^{-1}$ although $\Delta\nu_{\text{norm}}$ is 0.47 $\text{cm}^{-1}$. The pattern of the two components of the doublets fuse together, and as the field strength increases, the total width of this doublet pattern decreases. At 35,000 guass the whole pattern of the two lines is fused into one single broad line slightly less broad than the original no-field doublet. This appears to be a true Paschen-Back effect. No satellites splitting-off from one of the doublet componets as reported for the CH and OH bands have been found.

THE recent theoretical work of Hund[1], Kemble[2], and Van Vleck[3], has made the experimental determination of the exact effect of magnetic fields on certain characteristic band spectra a problem of some importance. It has been shown that there exist $S$, $P$, $D$, etc., molecular electronic levels with a spacing almost identical with those in corresponding atoms. The molecule has then in general a magnetic moment and should precess in a magnetic field. Those frequencies originating in the lowest rotational levels (the first line in each branch) should show a magnetic splitting comparable to the normal Zeeman effect in atomic lines. The change in energy produced by the field should be inversely proportional to $j^2$, and therefore in the great majority of band lines which represent rather large values of $j$ the splitting is probably so complicated and on such a small scale as to be undetectable. This explains why early investigators reported that band lines were insensitive to magnetic influence. The zero-point of a band was not at that time recognized as the

[1] F. Hund, Zeits. f. Physik **36,** 657 (1926) and **42,** 93 (1927).
[2] E. C. Kemble, National Research Council Bulletin, No. 57, pp. 326–353.
[3] J. H. Van Vleck, Phys. Rev. **28,** 980 (1926).

origin, and it is often masked by the lines of the branch returning from the head. Furthermore, the first line in each branch is always of low intensity, making exposure times of say 24 to 36 hours necessary when the field is applied to the source.

Most of the magnetic field effects so far reported for band lines are second-order effects akin to the Paschen-Back effect, such as the narrowing of doublets the splitting-off of satellite lines, and the production of wide doublets for lines having rather large $j$ values. And where a magnetic resolution for the lines near the origin has been noticed, the bands have not been of a simple type, so that second-order effects are usually present to complicate the situation. Curtis and Jevons[4], however, found that in the λ4659 helium band, a $^1P \rightarrow {}^1S$ transition, the only effect was the broading of the first lines in each branch. Also, Kemble and Mulliken[5] have recently obtained some fine results giving the Zeeman effect for the λ5610 CO band, a $^1S \rightarrow {}^1P$ transition. They find that the first lines of the $P$ and $Q$ branches become approximately half-normal triplets in confirmation of the Van Vleck formula based on the new quantum mechanics. The reader is referred to Kemble's article[2] for a discussion of all the Zeeman effect work on band spectra that had appeared up to that time.

We have used in this investigation a large Weiss-type, water-cooled magnet capable of producing field strengths up to 35,000 gauss in a 5 mm gap, the pole faces being 1 cm in diameter. A hydrogen atmosphere was maintained in a Back chamber fitting tightly onto the pole pieces, and the arc was struck parallel to the field. The fixed electrode was always a thin silver strip, while the vibrating electrode was of Al, Mg, etc. Since it was impossible to keep the arc chamber absolutely air-tight, it was necessary to have the hydrogen usually at atmospheric pressure, but a pressure of about 5 cm of hydrogen seemed to always yield more intense band spectra. Some of the spectrograms were taken in the second order of a 30-foot Littrow mounting 8 inch plane grating, while most of the exposures were in the second and third orders of the 21-foot Rowland grating. Exposure times ran from 6 hours for the AgH bands to 36 hours for the ZnH bands in the third order and with a Nicol in the path to test the polarization of the Zeeman components. It was possible to view the arc only in the direction perpendicular to the field. In all cases the electrodes had to be renewed at intervals during the exposure. Precautions were taken to maintain the temperature in the grating room practically constant.

## Silver Hydride Bands

The AgH bands in the near ultra-violet with the principal head at λ3330 (0−0 band) consist of single $P$ and $R$ branches, the $Q$ branches being entirely absent. They resemble closely the near infra-red HCl bands, and are classified according to Mulliken as a $^1S \rightarrow {}^1S$ transition. For both electronic levels, $\sigma_k$, the component of the orbital electronic angular momentum parallel to the

[4] W. E. Curtis and W. Jevons, Nature **116,** 746 (1925).

[5] See Note 35a, page 352, National Research Council Bulletin No. 57.

figure axis of the molecule, is zero, and consequently both levels should be non-magnetic. These bands should then be totally unaffected by magnetic fields of any strength, and experimental proof of this should form a verification of the assignment $^1S \rightarrow {}^1S$ to this type of band.

We, therefore, photographed these bands in the second order of the 21-foot grating, using field strengths of 10,000, 13,000, and 33,000 gauss. A close examination of the plates fails to reveal any difference between these spectrograms and that taken without a field. Moreover, the arc is just as easy to run with the full field as with no field, the exposure time of six hours giving in each instance lines of equal intensity. If there is a magnetic splitting or broadening of the lines, then obviously the required exposure time is lengthened considerably. In the $0-0$ band, unfortunately, the Ag arc line $\lambda 3349$ is very close to the zero-point and is necessarily overexposed, but the $R$ (3) and $P$ (3) lines are clear, and are seen to be absolutely unaffected by the magnetic field. It is to be concluded, then, that these bands are correctly represented as a $^1S \rightarrow {}^1S$ type.

## Aluminum Hydride Bands

The AlH $(0-0)$ band at $\lambda 4240$ consists of single $P$, $Q$, $R$ branches, and according to Mulliken is of a $^1P \rightarrow {}^1S$ type. Therefore, the Zeeman effect should be the same as in the CO $\lambda 5610$ band (a $^1S \rightarrow {}^1P$ transition) except that it is the lower electronic level which is non-magnetic in AlH. For a $^1P \rightarrow {}^1S$ transition, $\sigma_k' = 1$. $\sigma_k'' = 0$, and in both states $\sigma_s = s = 0$ and $\rho = 0$. Now Van Vleck,[6] using the new quantum mechanics, gives the formula

$$-r \cdot \sigma \cdot \kappa_n \cdot H/j(j-1) \tag{1}$$

for the change in energy produced by a magnetic field if there is rigid coupling of the spin electrons. The notation is that used by Kemble; $\kappa_n \cdot$ H is the normal Zeeman displacement, $r$ is the magnetic quantum number, $\sigma$ is the combined spin and orbital angular momentum in the direction of the figure axis, and $j$ is the total angular momentum quantum number. The Zeeman pattern for the lines of the AlH band should then be given by

$$\nu = \nu_0 + r' \cdot \kappa_n \cdot H/j'(j'+1) \tag{2}$$

where $r'$ assumes all integral values between $\pm j'$. Mulliken[7] gives $1\frac{1}{2}$ as the minimum value of $j'$, but the new mechanics value of $j$ is $\frac{1}{2}$ less than this. For $j' = 1$, $r'/j'(j'+1) = \pm\frac{1}{2}, 0$ so that the pattern for the first line in each branch should be a half normal triplet.

The first three lines in each branch are definitely broadened on all of our plates, but the resolution is not quite great enough to separate the components even with the highest field (34,000 gauss). The maximum spread of the pattern can be determined for these lines, however, and the results compared with the prediction of formula (2). The comparison is made in Table I. The theoretical values of the spread are computed by setting $r' = j'$

[6] J. H. Van Vleck, loc. cit., p. 1007.

[7] R. S. Mulliken, Phys. Rev. **28**, 1221 (1926).

in each case. For this field strength, a normal triplet would have a separation of 3.20 $cm^{-1}$ between the two outer components.

TABLE I

*Comparison between maximum spread of pattern and the theoretical separation.*

| Line | Plate 1. | Plate 2. | Plate 3. | Average | Theoretical value. |
|---|---|---|---|---|---|
| $R(1)$ | 0.976 $cm^{-1}$ | 1.158 $cm^{-1}$ | 0.910 $cm^{-1}$ | 1.015 $cm^{-1}$ | $1.60=\frac{1}{2}$ norm. |
| $R(3)$ | ——— | 0.862 | ——— | 0.862 | $0.80=\frac{1}{4}$ " |
| $Q(2)$ | 1.537 | 1.829 | ——— | 1.683 | $1.60=\frac{1}{2}$ " |
| $Q(3)$ | 1.239 | 1.421 | 1.190 | 1.283 | $1.07=\frac{1}{3}$ " |
| $Q(4)$ | 0.898 | 0.887 | 0.793 | 0.859 | $0.80=\frac{1}{4}$ " |
| $P(5)$ | 0.812 | 0.768 | 0.823 | 0.801 | $0.80=\frac{1}{4}$ " |

The agreement with the predicted values are, with the exception of the $R$ (1) line, fairly good. It is possible that the measurements on this line are vitiated by the presence of a foreign line, probably belonging to the secondary spectrum of hydrogen, and that consequently it should not be included in the table. It is apparent also that the correct $j$ values are those given by the new quantum mechanics, a half unit lower than those determined from the Kramers and Pauli formula. All of the higher members of each series in the band are apparently undisturbed by the magnetic field, which is just what you would expect if the spread of the pattern is inversely proportional to $j$. It is to be concluded, therefore, that these results are further confirmation of the correctness of Van Vleck's formula, and are a verification of the assignment $^1P\rightarrow{}^1S$ to the AlH bands.

## ZINC HYDRIDE BANDS

The bands of the ZnH system with a principal head at λ4326 (zero-point of the 0−0 band) are of a more complicated type, consisting of six branches, and are according to Mulliken a $^2P_1\rightarrow{}^2S$ transition. These bands have been analyzed by Hulthén,[8] and he also investigated their Zeeman effect for one field strength, 16,900 gauss. He reports some very curious "second-order" effects which may be briefly summarized as follows: The $P_1$ and $P_2$ branches show no effect, although overlapping of the first lines of the $P_2$ branch makes impossible a definite assertion about them. The first lines of the $Q_2$, $R_1$, and $R_2$ branches are split into wide doublets, but the higher members of these series show no effect. The $Q_1$ lines are split into wide doublets, measurable as far out as $Q$ (13). The separation of the two components of the doublets extrapolated to the origin has a value equal to twice the normal Zeeman effect.

Magnetic doublets of this character also occur for some lines in the hydrogen secondary spectrum, and as was first suggested by Kramers and Pauli,[9] must be due to loose coupling of the valence electron. Van Vleck[3] attributes this effect to a loose coupling of the spin axis of a valence electron in an excited state of the molecule. Because it is coupled loosely with the molecule,

[8] E. Hulthén, Thesis, Lund, 1923.

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

the spin axis orients itself either parallel or anti-parallel to the field, and consequently the energy is

$$E=E_0+2\sigma_s \cdot h \cdot \kappa_n \cdot H \tag{3}$$

where $\sigma_s = \pm\frac{1}{2}$ is the component of the electron's spin angular momentum parallel to the figure axis, and $\kappa_n \cdot$ H is the normal Zeeman separation. This loose coupling occurs only in the P state, and consequently will give a Zeeman displacement of the normal amount but with the central component lacking.

We have photographed the λ4326 ZnH band in the third order of the 21-foot Rowland grating with various field strengths ranging from 5,000 to 34,000 gauss. At 15,000 gauss our measurements check those given by Hulthén quite closely. The doublet separations for the $Q_1$ and $Q_2$ branches are given in Table II. The normal Zeeman displacement at this field strength is 0.71 $cm^{-1}$.

TABLE II

*Doublet separations for the $Q_1$ and $Q_2$ branches*

| Line | $\Delta\nu$ | Line | $\Delta\nu$ |
|---|---|---|---|
| $Q_1$ (8) | 1.34 $cm^{-1}$ | $Q_2$(2) | 1.51 $cm^{-1}$ |
| (9) | 1.05 | (3) | 1.37 |
| (10) | 1.10 | (4) | 1.50 |
| (11) | 0.97 | | |
| (12) | 1.08 | | |
| (13) | 1.11 | | |

Using this same field strength, we photographed the band through a Nicol prism set first with its plane of transmission parallel to the field and then perpendicular to the field. In both cases the $Q_1$ doublets appeared. It is to be inferred either that the two components are circularly polarized or that they are in reality quartets with very small separation between the outer components. The latter is the more attractive of the two alternatives, since the arc is being viewed perpendicular to the field. It is evident, however, that formula (3) does not exactly fit the facts, and that a more detailed theoretical treatment would be desirable.

Furthermore, a plate taken with a field strength of 34,000 gauss reveals the fact that these doublets tend to draw together at high fields. The $P_1$ and $P_2$ lines apparently remain unaffected even at this highest field. Here again are facts not explained by the theory.

As pointed out by Van Vleck,[10] in the case of this loose coupling of the spin axis, the situation must be that of Hund's case $b$[11] in which the spin axis is quantized relative to $j_k$. ($j_k$ is the resultant of $\sigma_k$ and $m$). A weak field would not be able to destroy this coupling, and according to Hund[11] the Zeeman components would be spaced a distance $1/j$ times the normal separation. But when the applied field becomes fairly strong, this internal coupling

[10] J. H. Van Vleck, loc. cit., p. 1010.

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

should be broken, and the close components should be merged into the wide doublets. Looking for this transition, we have photographed the bands with fields from 5,000 gauss up. Since for the small currents, the iron of the magnet is far from saturation, it is important that the current be held absolutely constant during the exposure. These exciting currents were therefore taken from a large 150 volt storage battery rather than the ordinary D. C. supply. We were not able to detect any Zeeman effect on the first $Q_2$ and $R$ lines, however, at field strengths below that necessary to give the wide doublets. That is, when the field strength becomes strong enough to give a measurable Zeeman effect, the internal coupling is apparently already broken down. Hund mentions the possibility of this predicament.

### Magnesium Hydride Bands

The MgH system with a principal head at λ5211 is classified as $^2P_{1,2} \rightarrow {}^2S$. The $P$, $Q$, and $R$ branches all consist of narrow doublets, the doublet separation being about 2 $cm^{-1}$ except near the origin where it becomes somewhat larger. With a field of 10,000 gauss all of the lines show a broadening, but there is not sufficient resolution on our plates to determine the Zeeman components. The lines near the origin have quite a spread, that for the $P_1$ (5) line being 1.56 $cm^{-1}$, although the separation of the two outer components of a normal triplet at this field strength is only 0.94 $cm^{-1}$. The doublets are fused together, the total separation between the extreme limits of the two patterns being somewhat greater than the original doublet separation. But as the field strength increases, the total width of this doublet pattern decreases, until at the highest field it is equal to or slightly less than the no-field separation between the two lines. The whole pattern is fused into one single broad line. This appears to be a true Paschen-Back effect, since a first order fine-structure is evidently present for moderate field strengths. Kemble[12] predicts exactly this effect, which has apparently not been observed before.

It is possible that with higher resolution and working under better conditions, among the most important of which would be a reduced pressure of the hydrogen in the arc chamber, the fine-structure of some of the Zeeman patterns in this MgH band could be observed. The wave-length region (λ5200) is more favorable than that for the other bands reported in this paper. There is no evidence of the existence of satellites splitting-off from the main lines under the influence of the magnetic field, such as Hulthén[8] and Fortrat[12] report for the CH and OH bands respectively.

Ryerson Physical Laboratory,
University of Chicago,
August, 1927.

[12] E. C. Kemble, loc. cit., p. 349.
[13] R. Fortrat, J. de physique et le rad. **5**, 20 (1924).