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The Zeeman effect in molecular doublet-doublet transitions in the « high field-low field » limit

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Résumé. — On a calculé les profils Zeeman des raies dues aux transitions moléculaires électroniques doublet-doublet, soit permises soit interdites en absence de couplage spin-orbite, pour les toupies asymétriques, dans le cas où à champ nul la séparation entre les doublets de spin est beaucoup plus forte dans l'un des deux niveaux responsables de la transition que dans l'autre. Il y a alors un intervalle des valeurs du champ magnétique appliqué où on peut considérer le spin électronique et la rotation moléculaire couplés dans le premier niveau, et découplés par le champ dans le deuxième. On peut prédire *a priori* les fréquences et les intensités des composantes Zeeman dans la situation considérée, que nous appelons « limite du champ fort-faible ».

On a montré que les profils Zeeman des raies dépendent surtout des règles de sélection relatives à la branche du spectre qu'on considère. En fait, les raies avec $\Delta N = \Delta J$ ont un maximum central tandis que les raies avec $\Delta N = \Delta J \pm 1$ ont une forme de selle, quelle que soit la polarisation de la lumière. On rencontre le premier type de branches pour les transitions qui sont permises en absence de couplage spin-orbite, et le deuxième type pour les transitions avec $\Delta N = \pm 2$ qui sont interdites en l'absence de couplage spin-orbite. Les deux types de profils sont mélangés dans toutes les autres branches correspondant à des transitions interdites en l'absence de couplage spin-orbite.

Abstract. — Zeeman line profiles for spin-allowed and forbidden electronic doublet-doublet transitions of molecular asymmetric tops have been computed for the case in which one of the combining states has a much larger zero-field splitting than the other. In such cases there must exist a range of external fields which are weak with respect to the high zero-field splitting state and strong with respect to the low zero-field splitting state. The respective Zeeman effects are therefore close to the weak-field limit of a strongly coupled state and the strong-field, uncoupled limit (Paschen-Back effect) of the weakly coupled state.

Zeeman component frequencies and intensities have been calculated for this « high field-low field » limit, and Zeeman pattern profiles of lines are seen to depend mostly on branch selection rules. Lines with $\Delta N = \Delta J$ show a central maximum, whereas lines with $\Delta N = \Delta J \pm 1$ exhibit a saddle shape, regardless of light polarization. The former type of lines occurs in spin-allowed transitions, the latter in the $\Delta N = \pm 2$ branches of spin-forbidden transitions. The two types of shape are mixed together in the remaining branches of spin-forbidden transitions.

1. Introduction. — In a previous article, we reported computed Zeeman line profiles of doublet-doublet ro-vibronic transitions in asymmetric tops at various field strengths [1]. Profiles could be easily predicted in the low field and high field limits, the eigenfunctions being those of the coupled (case b) and space fixed uncoupled (Paschen-Back) representations respectively.

In order to complete the survey of all possible cases, we consider here the features of the Zeeman effect when the zero-field splittings of the combining doublet states are very different from each other : in such cases we should expect there to be field values which will be « high » for the state with small zero-field splitting and « low » for the other one. We shall refer to such a situation as the « high field-low field » limit.

Notation and conventions are the same as in [1].

An actual case of interest is to be found in the visible spectrum of NO_2 , where the zero-field splittings in the upper states are markedly larger than in the ground state [2], to the extent that in the latter it can be in many instances disregarded [3].

2. Theory. — The eigenvalues for the « high field-low field » limit correspond in a good approximation to the diagonal elements of the ro-vibronic Zeeman energy matrices in the appropriate limiting representations, reported in [1] and [4]. Line frequencies of the magnetic components in a transition between a ground state « uncoupled », because of its small zero-field splitting, and a « coupled » upper state (Hund's near case b), only slightly perturbed by the field because of its large zero-field splitting, are reported in table I.

Table I. — « High field-low field » approximate frequencies in doublet-doublet transitions. $F'' = (F_1'' + F_2'')/2$.

$N' - J'$	F'	M_S''	Frequencies
- 1	F_1'	1/2	$F_1' - F'' + g\beta H [1/2 - M_J'/(2 N' + 1)]$
- 1	F_1'	- 1/2	$F_1' - F'' - g\beta H [1/2 + M_J'/(2 N' + 1)]$
1	F_2'	1/2	$F_2' - F'' + g\beta H [1/2 + M_J'/(2 N' + 1)]$
1	F_2'	- 1/2	$F_2' - F'' - g\beta H [1/2 - M_J'/(2 N' + 1)]$

The coupled components are designated by the well known symbols F_1 and F_2 , and the uncoupled components by the value of the quantum number M_S , representing the projection of the spin angular momentum on the space-fixed Z-axis.

It will be assumed throughout this article that the zero-field splitting is larger in the upper state. The reverse situation can be easily accommodated by interchanging the indices ' and '' and inverting the signs in all the expressions for relative energies. It is assumed that

$$\Delta(F_1''(N) - F_2''(N))$$

in the ground state can be disregarded.

The width of each of the four profiles in table I, applying the same approximations as in [1], is easily found to be about $g\beta H$; however, as the partners of each pair of lines involving the same F_1' or F_2' level are adjacent, two lines of width $2 g\beta H$ with their centres separated by $|F_1' - F_2'|$ are expected (see Fig. 1). These two lines clearly overlap if $|F_1' - F_2'|$ is less than $2 g\beta H$.

The prediction of line contours requires the knowledge of both line frequencies and intensities. In order to evaluate the latter, we shall make use of the intensity expressions of di Lauro [5], based on the case b (coupled) wavefunctions. Expansion of the field-uncoupled wavefunctions in the former basis gives :

$$\begin{aligned}
 |NM_N k\rangle |S = 1/2 \quad M_S = \pm 1/2\rangle = \\
 = \left(\frac{N \pm M_J + 1/2}{2N + 1} \right)^{1/2} |F_1\rangle \pm \left(\frac{N \mp M_J + 1/2}{2N + 1} \right)^{1/2} |F_2\rangle. \quad (1)
 \end{aligned}$$

Fig. 1. — Line widths and shapes in the « high field-low field » Zeeman effect in doublet-doublet transitions. The coefficients of the intensity expressions (2) are reported against M_J for all values of $\Delta N - \Delta J$. See text.

Thus the squares of the « high field-low field » transition moments, in terms of case b line strengths, are :

$$\begin{aligned} & \left| \left\langle M''_S = \pm \frac{1}{2} \left| \mu_F \right| F'_\alpha \right\rangle \right|^2 = \\ & = \left| \left(\frac{N'' \pm M''_J + 1/2}{2N'' + 1} \right)^{1/2} \langle F'_1 | \mu_F | F'_\alpha \rangle \pm \left(\frac{N'' \mp M''_J + 1/2}{2N'' + 1} \right)^{1/2} \langle F'_2 | \mu_F | F'_\alpha \rangle \right|^2 \quad (2) \end{aligned}$$

with $\alpha = 1, 2$.

Consideration of the dependence on M''_J of the magnitude of the coefficients in (2) leads to the result that combinations with $\Delta N = \Delta J$, whose zero-field oscillator strength comes from $F'_1 \leftrightarrow F''_1$ and $F'_2 \leftrightarrow F''_2$ transitions, tend to generate profiles with a single central maximum, whereas combinations with $\Delta N = \Delta J + 1$ and $\Delta N = \Delta J - 1$, related to $F'_2 \leftrightarrow F''_1$ and $F'_1 \leftrightarrow F''_2$ transitions respectively, tend to generate profiles with a saddle shape. This is illustrated in detail in figure 1.

Although the actual Zeeman profiles are affected also by the M_J dependence of $\langle F'_1 | \mu_F | F'_\alpha \rangle$ and $\langle F'_2 | \mu_F | F'_\alpha \rangle$, they are found to follow the patterns of figure 1 and to be independent of light polarization. This means that the above mentioned effect is dominant in determining the intensity distribution over the Zeeman components. This effect can be therefore of diagnostic interest.

3. Computed Zeeman profiles. — Figure 2 shows the profiles of a spin-allowed transition for fields from zero to 5.5 kG. The zero-field splitting were purposely chosen to be zero in the ground state and 0.235 cm^{-1} in the excited state, as in the ${}^{\text{a}}\text{R}(N = 15)$ and ${}^{\text{a}}\text{P}(N = 15)$ doublets of the $6475 \text{ \AA}$ band of NO_2 illustrated by Brand *et al.* [4].

At 0.5 and 1 kG, which represent approximately a « high field-low field » with these parameters, it is evident that the line centres are not displaced, as predictable from [1] in a case where F'_1 and F'_2 are almost degenerate. The intensity of spin-allowed transitions is mostly due to combinations with $\Delta N = \Delta J$, and the profiles at 0.5 and 1 kG consistently show a single central maximum with any light polarization. The Zeeman lines at 1 kG overlap each other to some extent (case with $|F'_1 - F'_2|$ less than $2g\beta H$). Brand and coworkers measured the Zeeman

Fig. 2. — Zeeman profiles of a spin-allowed doublet-doublet transition with $\Delta N = \Delta J = \pm 1$ and $\Delta K = 0$. $|F'_2 - F'_1| = 0.235 \text{ cm}^{-1}$ and $F''_1 = F''_2 = F''$. See text.

effect on doublets of the $5\,935 \text{ \AA}$ and of the $6\,475 \text{ \AA}$ bands of NO_2 with fields ranging from 2.5 to 5.5 kG, observing that the doublets coalesce filling the interval between the frequencies of the zero-field lines, with a resulting width of $|F'_1 - F'_2|$. Our calculations reproduce nicely the observed effect for these medium and high fields, considering that the experimental apparatus of [4] would not allow the observation of the tiny side features calculated at 2.5 kG, nor the details of the Zeeman profiles which would require more sophisticated techniques to be investigated.

Figure 2 clearly shows that high field Zeeman profiles depend on light polarization whereas « high field-low field » profiles depend only on whether the dominant contribution to the intensity of a given line comes from a $\Delta N = \Delta J$ or from a $\Delta N = \Delta J \pm 1$ combination, the first one being always dominant in spin-allowed transitions.

This effect becomes clearer in figure 3, where the Zeeman effect on spin-forbidden transitions with both $\Delta N = \Delta J$ and $\Delta N = \Delta J \pm 1$ intensity contributions is examined.

Figure 3a shows the profile of a $\Delta N = 2$ line, whose intensity comes from a $F'_1 \leftrightarrow F'_2$ combination, with $\Delta N = \Delta J + 1$. The saddle shape is evident in either polarization.

Fig. 3. — 1 kG profiles of a y -polarized spin-forbidden doublet-doublet transition with $\Gamma_{(ev)'} \times \Gamma_{(ev)''} = B_{1u}$ in D_{2h} , with $K' - K'' = 2$. The zero-field splittings are $|F'_2 - F'_1| = 0.400 \text{ cm}^{-1}$ and $|F''_2 - F''_1| = 0.020 \text{ cm}^{-1}$. $F'' = |F''_2 + F''_1|/2$.

The $\Delta N = 1$ transition to F'_1 of figure 3b involves one active $F''_1 \leftrightarrow F'_1$ combination with $\Delta J = \Delta N = 1$, and shows a profile with a central maximum.

In the case of spin-forbidden lines with mixed $\Delta N = \Delta J$ and $\Delta N = \Delta J \pm 1$ character, the « high field-low field » profile can be predicted only by calculation, unless one of the contributions to the intensity is known to be dominant. This is the case with the remaining lines of figure 3, whose profile depends on the relative magnitude of these two contributions. The $\Delta N = \Delta J + 1$ contribution is dominant in the transition to F'_2 of figure 3b, as can be deduced from the intensity expressions of [5], and the profile clearly exhibits a saddle.

In the high field limit three broad lines occur for spin-forbidden lines, all of width $|F'_2 - F'_1|$, consistently with [1].

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