Notes on G-factor of $\Pi_{1/2}$ molecules (1 June 2005 — 1st July 2005)

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1. Here I use my old notes to check Neil's conditions for G-factor of a $\Pi_{1/2}$ molecule to turn to zero.

The spin-rotational Hamiltonian of the $\Pi_{1/2}$ molecule in the external fields $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mathcal{B}}$ has the form [Kozlov and Labzowski (1995)]

$$H_{sr} = B\boldsymbol{J}^2 + \Delta \boldsymbol{S}' \cdot \boldsymbol{J} - D\boldsymbol{n} \cdot \boldsymbol{\mathcal{E}} + \mu_B \boldsymbol{S}'\hat{\boldsymbol{G}}\boldsymbol{\mathcal{B}}, \tag{1}$$

where G-tensor is diagonal in the molecular frame ($G_{xx} = G_{yy} = G_\perp$, $G_{zz} = G_\parallel$).

In the absence of the external fields, the eigenstates of this Hamiltonian are the states of a definite parity p:

$$|J, M, p\rangle = 1/\sqrt{2}\left(|J, M, \Omega = \tfrac{1}{2}\rangle + \chi p |J, M, \Omega = -\tfrac{1}{2}\rangle\right), \tag{2}$$

where the phase factor $\chi \equiv (-1)^{J+1/2}$. Corresponding eigenvalues are:

$$E_{J,p} = BJ(J+1) + \tfrac{\Delta}{4}\chi p(2J+1). \tag{3}$$

Magnetic moment $\boldsymbol{\mu} = -\mu_B \hat{\boldsymbol{G}}\boldsymbol{S}'$ has the following matrix elements on states (2):

$$\langle J, M, p|\mu_0|J, M, p\rangle = -\frac{\mu_B M}{4J(J+1)}\left[G_\parallel + (2J+1)\chi p G_\perp\right], \tag{4a}$$

$$\langle J, \tfrac{1}{2}, p|\mu_1|J, -\tfrac{1}{2}, p\rangle = \frac{\mu_B(2J+1)}{8\sqrt{2}J(J+1)}\left[G_\parallel + (2J+1)\chi p G_\perp\right]. \tag{4b}$$

We see that effective G-factor is the same for the parallel ($q = 0$) and perpendicular ($q = \pm 1$) components of the magnetic moment: $G_{\mathrm{eff},p} = G_\parallel + (2J+1)\chi p G_\perp$. This is not surprising as the choice of the quantization axis is arbitrary and G-factor should not depend on the direction of the magnetic field.

Electric field mixes states with $p = \pm 1$ and in a strong field limit instead of states (2) we have states with definite Ω, $|J, M, \Omega\rangle$. Note that in the absence of magnetic field the states $|J, M, \Omega\rangle$ and $|J, -M, -\Omega\rangle$ are degenerate Within the degenerate subspace the matrix elements of the magnetic moment are given by:

$$\langle J, M, \Omega|\mu_0|J, M, \Omega\rangle = -\frac{\mu_B M}{4J(J+1)} G_\parallel, \tag{5a}$$

$$\langle J, \tfrac{1}{2}, \tfrac{1}{2}|\mu_1|J, -\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \frac{\mu_B(2J+1)}{8\sqrt{2}J(J+1)} G_\perp. \tag{5b}$$

Now quantization axis is defined by the electric field and effective G-factor depends on the direction of the magnetic field. If magnetic field is parallel to the electric field, $G_{\mathrm{eff},\Omega} \approx G_\parallel$, while for the perpendicular field $G_{\mathrm{eff},\Omega} \approx G_\perp$.

1.1. **Magnetic field along the direction of electric field.** Equations (4a) and (5a) show that in a strong field limit both levels of the Ω-doublet have the same G-factor $G_{\mathrm{eff},\Omega} \approx G_{\|}$, while in the low field limit the levels of the Ω-doublet have G-factors $G_{\mathrm{eff},p} \approx G_{\|} + (2J+1)\chi p G_{\perp}$.

If effective G-factors in the low field and the high field limit are of the opposite sign,

$$G_{\|}\left[G_{\|} + (2J+1)\chi p G_{\perp}\right] < 0, \tag{6}$$

there is a field, where G-factor is zero. For the lowest spin-rotational state $J = \frac{1}{2}$ and $\Delta\chi p < 0$ [see Eq. (3)]. Condition (6) here is reduced to

$$\begin{cases} \left|\frac{2G_{\perp}}{G_{\|}}\right| > 1, \\ \Delta G_{\|} G_{\perp} > 0. \end{cases} \tag{7}$$

These equations agree with Neil's conclusions.

1.2. **Magnetic field perpendicular to electric field.** Now we use equations (4b) and (5b). Again, in a strong field limit both levels of the Ω-doublet have the same G-factor $G_{\mathrm{eff},\Omega} \approx G_{\perp}$, while in the low field limit G-factors of the Ω-doublet are the same.

For this geometry the condition for G-factor to turn to zero for some electric field is:

$$G_{\perp}\left[G_{\|} + (2J+1)\chi p G_{\perp}\right] < 0. \tag{8}$$

For the lowest spin-rotational state $J = \frac{1}{2}$ and $\Delta\chi p < 0$ Eq. (8) has two solutions:

$$\begin{cases} \left|\frac{2G_{\perp}}{G_{\|}}\right| > 1, \\ \Delta > 0. \end{cases} \tag{9a}$$

$$-1 < \frac{2G_{\perp}}{G_{\|}} < 0. \tag{9b}$$

1.3. **Discussion.** We see that conditions (7) and (9) are different. The former condition is fulfilled for PbF, while the latter is not. Even when both conditions are fulfilled, the field at which G-factor turns to zero depends on the geometry. Therefore, we can not choose electric field in such a way that magnetic effects disappear completely.

If the degenerate subspace consists of two levels with the projections of the angular momentum $M = \pm\frac{1}{2}$, these levels are mixed by the magnetic moment operator in the first order. This leads to the splitting of the order of $\mu_0 G_{\mathrm{eff}} \mathcal{B}_{\perp}$.

Fortunately, PbF molecule has at least one nonzero nuclear spin (Pb has mostly spinless isotopes, $I_1 = 0$, but F has only one isotope with $I_2 = \frac{1}{2}$). Because of that we have to include nuclear spin into consideration. In the electric field we still have twofold degeneracy of all levels with $M_F = M + M_{I_2} \neq 0$. If we choose hyperfine component of the ground state with $M_F = \pm 1$, then magnetic field can mix two degenerate levels only in the second order via the level with $M_F = 0$. In this case the splitting caused by the perpendicular component of the magnetic field is suppressed by the factor $(\mu_0 G_{\mathrm{eff}} \mathcal{B}_{\perp})/\Delta_{0,1}$, where $\Delta_{0,1}$ is the hyperfine splitting between levels with $M_F = 0$ and $M_F = \pm 1$. The hyperfine constants for the fluorine are not known reliably, but we can estimate $\Delta_{0,1}$ to be of the order of 10^8 Hz.

Let us estimate the splitting for the magnetic field induced by the motion of the molecule with $v = 500$ m/sec in the field 5×10^4 V/cm:

$$\mathcal{B}_\perp = \frac{v}{c}\,\mathcal{E} \approx 3 \times 10^{-4}\,\mathrm{Gs}.$$

Corresponding splitting is of the order of

$$\delta_v \sim \begin{cases} \mu_0 G_\perp \mathcal{B}_\perp & \sim \quad 10^2 \text{ Hz}, \quad \text{for } |M_F| = \frac{1}{2}, \\ (\mu_0 G_\perp \mathcal{B}_\perp)^2/\Delta_{0,1} & \sim \quad 10^{-4} \text{ Hz}, \quad \text{for } |M_F| = 1. \end{cases} \tag{10}$$

This estimate shows that hyperfine splitting may solve the problem with motional magnetic field.

2. Why $G_\perp$ and $G_\parallel$ are what they are?

Hamiltonian (1) accounts for the spin-orbital mixing between $\Pi_{1/2}$ and $\Sigma_{1/2}$ states [Kozlov et al. (1987)]. For a pure $\Pi_{1/2}$ state $\Delta = G_\perp = G_\parallel = 0$. For a mixed state $|\Omega = \frac{1}{2}\rangle$,

$$|\tfrac{1}{2}\rangle = \xi|\Pi_{1/2}\rangle + \eta|\Sigma_{1/2}\rangle, \tag{11}$$

we get:

$$G_\parallel = 2\eta^2, \tag{12a}$$

$$G_\perp = 2\eta\xi L + 2\eta^2, \tag{12b}$$

$$\frac{\Delta}{2B} = 2\eta\xi L + \eta^2, \tag{12c}$$

where $L \equiv \langle \Pi | L_x + iL_y | \Sigma \rangle$. We see that within this model $G_\parallel > 0$ and $\frac{\Delta}{2B} = G_\perp - \frac{1}{2}G_\parallel$.

If spin-orbital mixing $|\eta| \ll 1$, $\frac{\Delta}{2B} \approx G_\perp$ and $\Delta G_\perp G_\parallel > 0$. In order to get the opposite sign of this product we need $-1 < \frac{\xi}{\eta}L < -\frac{1}{2}$. Typically $L \sim 1$ and to meet this condition we need $\eta \sim \xi \sim 1$.

Conditions (7) are automatically met by the model (11) with small spin-orbital mixing $|\eta| \ll 1$. This conclusion holds even when several Σ states are mixed with a given Π state. Indeed, we can take Σ function in (11) to be any linear combination of physical Σ states of a molecule. Therefore, it seems unlikely that correlations can break relations (7). On the other hand, the values of the mixing η and of the matrix element L can change when correlations and spin-orbit interaction are included more accurately, than it was done by Kozlov et al. (1987). Then, equations (12) will give different values for G-factors. That, in turn, will change the critical field, where $G_{\mathrm{eff}} = 0$.

3. Conclusions

Conditions (7) are likely to hold for PbF. Therefore, for the parallel magnetic field the ground state G-factor turns to zero for some critical field. This field depends on G-factors, which are not known accurately enough to calculate this field reliably. For the perpendicular magnetic field G-factor never turns to zero and is of the order of $G_\perp$. However, if the experiment is done on the hyperfine levels with $|M_F| = 1$, there is strong suppression of the splitting caused by the perpendicular field.

References

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