Alignment-orientation conversion in molecules in an external magnetic field caused by a hyperfine structure

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Abstract. The paper presents a discussion on the problem of alignment-orientation conversion in an excited state of molecules. It is shown that a rather strong alignment-orientation conversion effect in the excited molecular state can be caused by a joint action of an external magnetic field and hyperfine interaction. The orientation thus created is transverse, *i.e.* perpendicular to the direction of the external magnetic field. The magnitude of this effect is analyzed as dependent on molecular parameters.

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1 Introduction

Usually, if an ensemble of atoms or molecules is excited by linearly polarized light the spatial distribution of angular momentum of excited state particles possesses alignment. That means that the cylindrical symmetry of excitation light polarization vector **E**, that can be characterized by a double-head arrow ⟸⟹, is transferred to the ensemble of atoms or molecules.

An interest about processes, that can break this symmetry and cause alignment-orientation conversion has been alive already for a long time. As a result, one may expect an appearance of angular momentum distribution that can be characterized by a single-head arrow ⟹. Experimentally appearance of an orientation can be detected as an emergence of circularly polarized fluorescence from such an ensemble of particles.

The possibility of conversion from alignment to orientation under the effect of anisotropic collisions was first considered by Lombardi [1] and Rebane [2]. They have shown that partial alignment-orientation conversion in an ensemble of atoms may be induced by anisotropic collisions when the angle between the direction of these anisotropic collisions and that of alignment differs from 0 or $\pm\pi/2$. The theoretical prediction was soon after confirmed in experimental observation [3,4].

The other group of works deals with electric field effects. Lombardi [5] described a circularity signal from He in a high-frequency capacitative electrodeless helium discharge. Necessary initial alignment in this case was produced by joint action of collisions with electrons and action of an external field. The electric field of the discharge was considered as a perturbing factor able to produce an orientation signal. Later the alignment-orientation

conversion caused by external electric field leading to quadratic Stark effect in atoms or molecules was considered in great detail in [6–8]. This effect was suggested to be used to orient molecules selectively in beam experiments [9]. Recently alignment-orientation conversion in an electric field was utilized for measuring permanent dipole moments and Λ-doubling constants in NaK molecules [10].

In general, the main reason why an electric field is able to convert alignment into orientation is because an electric field is characterized by a polar vector. At the same time it is known that magnetic field, which is characterized by an axial vector can not change the symmetry of angular momentum distribution.

However, this obstruction can be circumvented if in addition to the linear Zeeman effect there exist any perturbing factors causing slight non-linearity in the primarily linear Zeeman effect. For example, as such a perturbing factor can serve hyperfine interaction in atoms or molecules. For the first time alignment-orientation conversion as a result of hyperfine interaction was predicted theoretically [11] and demonstrated experimentally by Lehmann [12]. He studied optical pumping of a diamagnetic ground state of atoms possessing magnetic hyperfine structure. Atoms were excited by an unpolarized light beam in presence of an external magnetic field. Joint action of hyperfine interaction and the external magnetic field directed along the unpolarized exciting light beam caused appearance of a *longitudinal* (along the magnetic field direction) orientation. This effect can be considered as a kind of magnetic dichroism.

Vigué with his colleagues studied theoretically as well as measured experimentally in an iodine molecule the appearance of a *longitudinal* orientation in an external magnetic field as a result of predissociation [13–15]. Such orientation can take place as a direct consequence of interference between magnetic and natural predissociation.

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Not so long time ago it was shown theoretically as well as demonstrated experimentally that an external magnetic field can slightly mix together molecular states with opposite parity and, as a result, can cause the appearance of *transverse* orientation (perpendicular to the direction of the external field) from an initially aligned ensemble of molecules. It needs for this that the initial alignment is created in a direction differing from 0 or $\pm\pi/2$ with respect to the external field and that the intramolecular interaction-caused Zeeman effect deviates slightly from a linear one [16,17].

In this paper we will demonstrate that the external magnetic field in the presence of hyperfine interaction can cause the appearance of a *transverse* orientation as well. In other words, we will demonstrate that the hyperfine structure (HFS) in an external magnetic field can cause the appearance of a kind of magnetic birefringence.

2 Orientation of the molecules

An easy way to characterize the angular momentum distribution in an ensemble of atoms or molecules consists in applying an angular momentum quantum density matrix. Let us consider a molecule possessing hyperfine structure which is placed in an external magnetic field. Let us further assume that angular momentum alignment in the excited state of this molecule is created by an absorption of linearly polarized light with an arbitrarily directed $\mathbf{E}$ vector. In this situation the density matrix, that characterizes coherence between magnetic sublevels with quantum numbers M and M' for an ensemble of molecules in an excited state can be calculated as [18]

$$^{kl}f_{MM'} = \frac{\widetilde{\Gamma}_p}{\Gamma + \mathrm{i}^{kl}\Delta\omega_{MM'}}$$
$$\times \sum_{j\mu} \langle\gamma_k M|\,\widehat{\mathbf{E}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle \langle\gamma_l M'|\,\widehat{\mathbf{E}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle^* . \quad (1)$$

In this equation $\widetilde{\Gamma}_p$ is a reduced absorption rate, Γ is the excited state relaxation rate and $^{kl}\Delta\omega_{MM'}$ is the splitting of magnetic sublevels M and M' belonging to the excited state levels k and l. Magnetic quantum numbers of the ground state level η_j are denoted by μ and the magnetic quantum numbers of the excited state level γ_k by M or M'.

In an external magnetic field the ground and excited state levels η_j and γ_k are not characterized any more by total angular momentum quantum numbers F'' and F' respectively, but are mixture of these states

$$|\gamma_k M\rangle = \sum_{F'=J'-I}^{F'=J'+I} C_{kF'}^{(\mathrm{e})}\,|F',M\rangle,$$
$$|\eta_j\mu\rangle = \sum_{F''=J''-I}^{F''=J''+I} C_{jF''}^{(\mathrm{g})}\,|F'',\mu\rangle \quad (2)$$

created by an external field. $C_{kF'}^{(\mathrm{e})}, C_{jF''}^{(\mathrm{g})}$ are the wave function expansion coefficients that represent the expansion of the molecular state in a magnetic field over the wave functions of hyperfine levels in absence of an external field. The method for calculating these coefficients will be described further.

There are several methods how to tell whether or not a particular molecular state described by a density matrix (1) possesses orientation. One possibility is to expand this matrix over the irreducible tensorial operators. These expansion coefficients can directly be attributed to the alignments and the orientation of the molecular ensemble [7,19,20]. This method was used previously to analyze hyperfine interaction in the H_2 molecule and the influence of this interaction on the polarization of laser-induced fluorescence [21]. Another way which will be used in this paper is to calculate directly the fluorescence circularity rate

$$C = \frac{I(E_{\mathrm{left}}) - I(E_{\mathrm{right}})}{I(E_{\mathrm{left}}) + I(E_{\mathrm{right}})} \quad (3)$$

from the density matrix in spontaneous transition from a particular excited state of the molecule. $I(E_{\mathrm{left}})$ and $I(E_{\mathrm{right}})$ are the intensities of the fluorescence with opposite circularity, if detected at some certain direction from the source containing excited molecules. If circularity differs form zero, then it means that the ensemble of molecules in excited state possesses an orientation. This is a functional way of calculating orientation of molecules, because in experimental studies this is a most frequently used approach to registering the appearance of orientation in an ensemble of molecules or atoms, see for example [6].

Let us assume that we register spontaneous fluorescence with a spectral device which does not resolve hyperfine components, say, an ordinary monochromator. The intensity of the fluorescence with definite polarization characterized by a vector $\mathbf{E}_{\mathrm{f}}$ in a spontaneous transition from the excited state J', characterized by a set γ_k of levels in an external field, to the ground state J''_{final}, characterized by a set η_j of levels, can be calculated, according to [18], as

$$I(\mathbf{E}_{\mathrm{f}}) = I_0 \sum_{MM'\mu} \sum_{klj} \langle\gamma_k M|\,\widehat{\mathbf{E}}_{\mathrm{f}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle$$
$$\times \langle\gamma_l M'|\,\widehat{\mathbf{E}}_{\mathrm{f}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle^{*\,kl}f_{M'M}. \quad (4)$$

To calculate the matrix elements entering equations (1, 4) some technical problems must be solved. Matrix elements of type $\langle\gamma_k M|\,\widehat{\mathbf{E}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle$ can be easily expressed through the matrix elements defined by hyperfine levels of the molecular states in absence of an external field

$$\langle\gamma_k M|\,\widehat{\mathbf{E}}^*\!\cdot\!\widehat{\mathbf{D}}\,|\eta_j\mu\rangle = \sum_{F'F''} C_{kF'}^{(\mathrm{e})} C_{jF''}^{(\mathrm{g})} \langle F'M|\,\widehat{\mathbf{E}}^*\!\cdot\!\widehat{\mathbf{D}}\,|F''\mu\rangle .$$
$$(5)$$

To matrix elements defined by hyperfine states the Wigner-Eckart theorem [7,19,20] can be applied

$$\langle F'M| \widehat{\mathbf{E}}^* \cdot \widehat{\mathbf{D}} |F''\mu\rangle = \sum_q (E^q)^* (-1)^{F'-M}$$
$$\times \begin{pmatrix} F' & 1 & F'' \\ -M & q & \mu \end{pmatrix} \langle F'\| \widehat{D} \|F''\rangle . \quad (6)$$

Here, the light vector is represented by its components E^q in a cyclic system of coordinates [7,20]. Finally, the last reduced matrix element for an axially symmetric system, such as a diatomic molecule, can be written as [19]

$$\langle F'\| \widehat{D} \|F''\rangle = (-1)^{J'+I+F''+1} \sqrt{(2F'+1)(2F''+1)}$$
$$\times \begin{Bmatrix} J' & F' & I \\ F'' & J'' & 1 \end{Bmatrix} \langle J'\| \widehat{D} \|J''\rangle . \quad (7)$$

All this allows to calculate an angular momentum distribution in an excited state of a molecule with HFS, if it absorbs light of definite polarization **E** while placed in an external magnetic field. This angular momentum distribution is characterized by the excited state angular momentum density matrix $^{kl}f_{MM'}$ (Eq. (1)). In turn this density matrix allows to calculate the degree of circular polarization of the fluorescence from the ensemble of molecules and, as a consequence, to determine whether or not the ensemble of molecules possesses overall orientation.

Nevertheless, to carry out a simulation of the fluorescence circularity rate for a particular model situation we still need to find the energy splitting $^{kl}\Delta\omega_{MM'}$ of magnetic sublevels of excited state molecules in an external field and the wave function mixing coefficients $C_{kF'}^{(e)}, C_{jF''}^{(g)}$ entering equations (1, 2) respectively. The next section will describe how these quantities can be determined.

3 A molecule with HFS in an external magnetic field

The additional energy of a molecule with an electronic magnetic moment $\boldsymbol{\mu}_J$ and a nuclear magnetic moment $\boldsymbol{\mu}_I$ in an external magnetic field **B** can be written as

$$E_B = -\boldsymbol{\mu}_J \cdot \mathbf{B} - \boldsymbol{\mu}_I \cdot \mathbf{B}, \quad (8)$$

where the magnetic moments are connected with the respective angular moments **J** and **I** of a molecule

$$\boldsymbol{\mu}_J = -\frac{g_J \mu_B}{\hbar} \mathbf{J}, \qquad \boldsymbol{\mu}_I = -\frac{g_I \mu_0}{\hbar} \mathbf{I}. \quad (9)$$

We assume here that the Landé factor g for orbital motion of an electron is positive.

Molecular wave functions for a molecular rotational state with HFS created by one nucleus with nuclear spin quantum number I can be written as

$$|(JI) FM\rangle , \quad (10)$$

where F is the total angular momentum of the molecule with projection on the quantization axis z characterized by quantum number M.

The matrix elements of the respective Hamilton operator H_B can be written as

$$H_B = \langle (JI) FM| E_B |(J'I) F'M'\rangle$$
$$= \frac{g_J \mu_B}{\hbar} B \langle (JI) FM| \mathbf{J} |(J'I) F'M'\rangle$$
$$+ \frac{g_I \mu_0}{\hbar} B \langle (JI) FM| \mathbf{I} |(J'I) F'M'\rangle \quad (11)$$

where the operator in the first term acts only upon the electronic part of the wave function, but in the second term only upon the nuclei part of the molecular wave function.

Let us consider each term on the right-hand-side of (11) separately. In the $\langle (JI) FM| \mathbf{J} |(JI) FM\rangle$ operator acts only on the electronic part of the wave function. So, according to the Wigner-Eckart theorem [19,20], we have

$$\langle (JI) FM| J^0 |(J'I) F'M'\rangle = (-1)^{F-M}$$
$$\times \begin{pmatrix} F & 1 & F' \\ -M & 0 & M' \end{pmatrix} \langle (JI) F\| J^0 \|(J'I) F'\rangle , \quad (12)$$

and the reduced matrix element can be expanded further

$$\langle (JI)F\| J^0 \|(J'I)F'\rangle = (-1)^{J+I+F'+1} \sqrt{(2F+1)(2F'+1)}$$
$$\times \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix} \langle J\| J^0 \|J'\rangle . \quad (13)$$

For the last reduced matrix element we have

$$\langle J\| J^0 \|J'\rangle = \sqrt{J(J+1)(2J+1)}\delta_{JJ'} . \quad (14)$$

If we collect all terms together we arrive at

$$\langle (JI)FM| J^0 |(J'I)F'M'\rangle = (-1)^{J+I+F'+F-M+1}$$
$$\times \sqrt{(2F+1)(2F'+1)J(J+1)(2J+1)}$$
$$\times \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ -M & 0 & M' \end{pmatrix} \delta_{JJ'} . \quad (15)$$

In a similar way for second term we have

$$\langle (JI) FM| I^0 |(J'I) F'M'\rangle = (-1)^{J+I+F+F-M+1}$$
$$\times \sqrt{(2F+1)(2F'+1) I(I+1)(2I+1)}$$
$$\times \begin{Bmatrix} I & F & J' \\ F' & I & 1 \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ -M & 0 & M' \end{pmatrix} . \quad (16)$$

Besides, as part of the diagonal elements we have ordinary HFS. Magnetic dipole HFS

$$H_m = a\frac{1}{2}\frac{\Lambda^2}{J(J+1)} [F(F+1) - J(J+1) - I(I+1)], \quad (17)$$

a being a magnetic HFS constant, and the electric quadrupole HFS

$$H_q^{(0)} = b_0$$
$$\times \frac{[3 - J(J+1)][3X(X+1)/4 - J(J+1)I(I+1)]}{(2J-1)J(J+1)(2J+3)2I(2I-1)}$$
(18)

b_0 being the usual (longitudinal) electric quadrupole HFS constant. In addition to this

$$H_q^{(2)} = \pm b_2 \frac{\sqrt{3/2}[3X(X+1)/4 - J(J+1)I(I+1)]}{(2J-1)(2J+3)2I(2I-1)}$$
(19)

must be considered for Π state [22–24], where the $+$ sign stands for the e component and the $-$ sign for f components. In these equations $X = F(F+1) - J(J+1) - I(I+1)$. The HFS constant b_2 may be called a transversal HFS constant, because it is associated with the transversal irreducible component of the electric field gradient.

Energies of molecular states in an external field can be obtained by a standard procedure by diagonalization of the Hamilton matrix defined above. Besides, in a process of matrix diagonalization the coefficients defining the expansion of the wave function of state in the field over the hyperfine state wave functions can be obtained as well.

4 Example for NaK

To make calculations for a real molecule and to find out how large the effect of alignment-orientation conversion can be for a real system, one must know certain molecular constants. In particular one must know the orbital Landé factor g_J and the nuclear Landé factor g_I in equation (11) as well as the molecular hyperfine constants a, b_0, b_2 entering equations (17–19). Unfortunately, at least some of these quantities are not known for most of the molecules in excited state.

Nevertheless, in many cases the necessary molecular constants can be easily estimated with good accuracy from the known properties of the nucleus and atomic constants. In this section we are going to demonstrate how it can be done. As an example, let us consider the very simple and widely studied molecule – NaK in its excited D$^1\Pi$ state. We chose this heteronuclear molecule, because, as it will be shown further, for this molecule the assumption that only one nucleus creates HFS can be justified with certain accuracy. Of course, calculations can be also performed accounting for influence of both nuclei, but this would make calculations unnecessary complicated and exceeds the limits of the present paper.

Let us start with Landé factors. The most accurate values of the gyromagnetic ratio for nuclei of interest in Bohr magnetons are $g_I = -0.0008046108(8)$ for ^{23}Na and $g_I = -0.00014193489(12)$ for ^{39}K [25]. This means that the magnetic moment of Na is almost six times larger than that of K. The electron Landé factor in molecular $^1\Pi$ state can easily be calculated as $g_J = 1/[J(J+1)]$ [26].

Let us continue with HFS constants. The magnetic HFS constant a can be calculated as

$$a = 2g_I \mu_B^2 \sum_n \left(\frac{1}{r^3}\right)_{av},$$
(20)

where g_I is the Landé factor of a nucleus causing the HFS.

Let us estimate the magnitude of magnetic HF splitting constants a for both nuclei of NaK. As pointed out as early as in [27], the average of $(r^{-3})_{av}$ is taken over only those electrons which form the angular momentum of a molecule.

We know that the molecular D$^1\Pi$ state at large internuclear distance correlates with atomic states 3^2P for Na and 4^2S for K [28]. It means that in this approximation the K does not contribute to the molecular electronic angular momentum. For the atomic orbital of Na an estimation of $(r^{-3})_{av}$ can be done using alkali atom wave functions. This leads to [19]

$$\frac{1}{r^3} = \frac{Z_a^2 Z_i}{n_*^3 (l+1)(l+1/2)l}.$$
(21)

The parameters are $Z_a(\text{Na}) = 1$, $n_*^3(\text{Na}(3p)) = 2.12$, and $Z_i(\text{Na}) = 7.59$ [19]. Obviously, all these numerical values of constants allow us to conclude that at first approximation we can neglect the magnetic nuclear splitting caused by K and deal only with the effect caused by one nucleus, namely Na.

A direct way, how to estimate the HFS constant a for Na is to calculate equations (20, 21), and we arrive at $a = 37.3$ MHz. This estimate for the molecular a_{mol} can be cross-checked using data that can be obtained directly from the atomic hyperfine spectrum. From [27] we know the connection between atomic a_{at} and molecular a_{mol} constants

$$a_{mol} = a_{at} \frac{j(j+1)}{l(l+1)}.$$
(22)

From [25] we know the atomic magnetic HFS constants for Na $3P_{1/2}$, being $a_{1/2} = 94.3$ MHz and for $3P_{3/2}$ $a_{3/2} = 18.69$ MHz. Making use of (22) we get from two atomic constants $a_{mol} = 35.4$ MHz and $a_{mol} = 35.0$ MHz respectively. For final check we can use an experimental value of $\overline{r^{-3}}$ given in [27] explicitly for Na p electrons as 1.65×10^{24} cm^{-3}. Using this directly in formula (20), we again get the very close numerical value $a = 34.5$ MHz. The level of coincidence of a values for the NaK molecule, as estimated by different approaches gives us confidence in the value obtained. This means that we can use further the a value around 35 MHz relatively safely.

The magnetic HFS constants b_0 and b_2 can be calculated according to the expressions $b_0 = eQq_{11}$ and $b_2 = eQq_{-11}$, where e is the electron charge, Q is the nucleus quadrupole moment, and $q_{\Lambda\Lambda}$ and $q_{\Lambda-\Lambda}$ are the longitudinal and transversal electric field gradients respectively. The electric field gradient components q_{ij} can be calculated according to [22,24]

$$q_{\Lambda+\mu\,\Lambda} = 2N(-1)^\mu \langle -\Lambda - \mu \| eC_{-\mu}^{(2)}(\theta,\varphi)/r^3 \| -\Lambda \rangle,$$
(23)

where N is the number of electrons, and Λ is a quantum number that represents the angular momentum projection on the internuclear axis.

At first approximation we can assume that the molecular orbital consists of two atomic orbitals centered on each nucleus. Besides, a p orbital is centered on the Na atom, but on the K atom s one.

For Na we can write

$$|\Lambda\rangle = \psi_r(r) Y_{l\Lambda}(\theta, \varphi) \qquad (24)$$

and, using an explicit form for the operator $C_\mu^{(2)}(\theta, \varphi) = \sqrt{4\pi/5} Y_{2\mu}(\theta, \varphi)$, we can immediately obtain

$$q_{\Lambda+\mu\ \Lambda} = 2N(-1)^\mu e \langle\psi_r| r^{-3} |\psi_r\rangle \langle Y_{l\ -\Lambda-\mu}| C_{-\mu}^{(2)} |Y_{l\ -\Lambda}\rangle$$
$$= 2N(-1)^\mu e\overline{r^{-3}} C_{l020}^{l0} C_{l\ -\Lambda\ 2\ \mu}^{l\ -\Lambda+\mu}. \qquad (25)$$

The explicit form for Clebsch-Gordan coefficients allows us to have

$$q_{\Lambda\Lambda} = -\frac{2e}{5}\overline{r^{-3}}, \qquad q_{\Lambda-\Lambda} = -\sqrt{6}\frac{2e}{5}\overline{r^{-3}}. \qquad (26)$$

An important point here is that the average $\overline{r^{-3}}$ for these calculations is over all electrons, not only those contributing to an electron angular momentum, as it was in the case of magnetic HFS.

For an s orbital it immediately follows from formulae presented above that $q_{\Lambda\Lambda} = q_{\Lambda-\Lambda} = 0$. This means that at first approximation we can assume again that in a HFS of NaK in $D^1\Pi$ state only the Na nucleus contributes and that the ratio between electric HFS constants related to longitudinal $q_{\Lambda\Lambda}$ and transversal $q_{\Lambda-\Lambda}$ components of the electric field gradient can be obtained from (26).

Most precise data on nuclear quadrupole moments are available from [29]. Namely, $Q\left(^{23}\text{Na}\right) = +0.1006(20)$ b and $Q\left(^{39}\text{K}\right) = +0.049(4)$ b. As far as for closed shell electrons we have the electric field gradient $q = 0$, probably for estimates within the same accuracy range as in a case of magnetic constants we can put numerical values of $\overline{r^{-3}}$ for p electrons obtained in case of a in formulae $b = eQq_{\Lambda\Lambda}$. This gives us a first approximation for $b_0 = 2.64$ MHz. This value should be close to the experimental one for the Na atom in ^{2}P state, as it actually is. For the Na atom we have $b = 2.90$ MHz [25].

5 Analysis of the observable signals

The analysis performed above allows as to assume that, at first approximation hyperfine splitting of NaK molecule is caused only by the Na nucleus, with little influence from the K nucleus. The following parameters determine the HFS splitting: nucleus spin of Na $I = 3/2$, Landé factor for the Na atom $g_J = 0.5$, $g_I = -0.0008$. Hyperfine constants-magnetic dipole $a = 35$ MHz, electric quadrupole $b_0 = 3$ MHz, $b_2 = \sqrt{6}b_0$. The excited state relaxation rate for NaK in $D^1\Pi_u$ state is equal to 5×10^7 s^{-1} [24,30]. Diagonalization of the Hamilton matrix for the $^1\Pi$
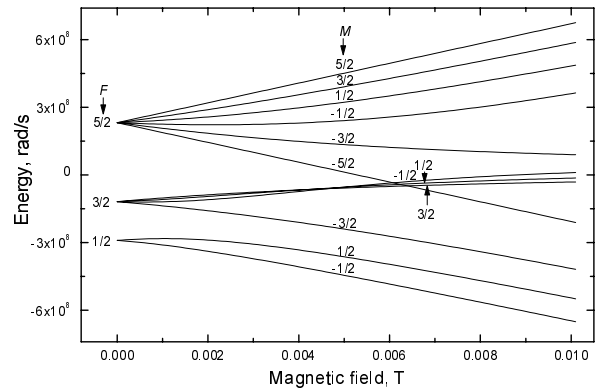

Fig. 1. HFS level splitting in an external magnetic field for excited molecular state with quantum numbers $J = 1$, $I = 3/2$. Other parameters see in the text.

excited state rotational level $J = 1$ yields the magnetic sublevel energies as dependent on the external magnetic field strength, as depicted in Figure 1. All level crossings are real, because in a model considered only levels with coinciding angular projection M values mutually interact. For levels with the same M but different F it would be anticrossing, in case they came close in the energy scale.

The considered magnetic field region corresponds to a situation when the field is of an intermediate strength. For a very low field strength each hyperfine level experiences linear Zeeman effect. As the field strength increases, we are coming to the region when the Zeeman energy is close to the hyperfine splitting energy and we have an energy level pattern that is most complicated. If the field is increased further, we arrive at a region when we see normal Zeeman splitting again (linear Zeeman effect) but in this case not for a hyperfine level, but for a rotational level J with quantum number equal to 1. The obtained energy level pattern allows us to calculate observable signals. As demonstrated in [6], one may expect an orientation signal with largest amplitude, if molecules are excited with linearly polarized light, with the light electric field vector at the angle $\pi/4$ with respect to the external field direction – the z-axis. Let us assume $\theta = \pi/4$ and $\varphi = 0$. To have a most pronounced signal one must observe circular polarization of fluorescence in the xy-plane. In our calculation we assumed that fluorescence circularity as defined by equation (3) is measured in the direction characterized by the angles $\theta = \pi/2$, $\varphi = \pi/2$.

Let us consider two possible transition types $J''_{\text{initial}} = 0 - J' = 1 - J''_{\text{final}} = 0$ and $J''_{\text{initial}} = 0 - J' = 1 - J''_{\text{final}} = 2$, where the rotational quantum numbers of the initial, excited and final state are shown. For these two types of transition simulated signals are presented in Figure 2.

As it may be seen, the signals reveal a remarkable amplitude. We can obtain angular momentum orientation that leads to the fluorescence circularity of several percents. It must be considered as a circularity rate which can be measured easily on simple setups [7]. Another important feature is that these signals have different signs (different directions of angular momentum orientation)
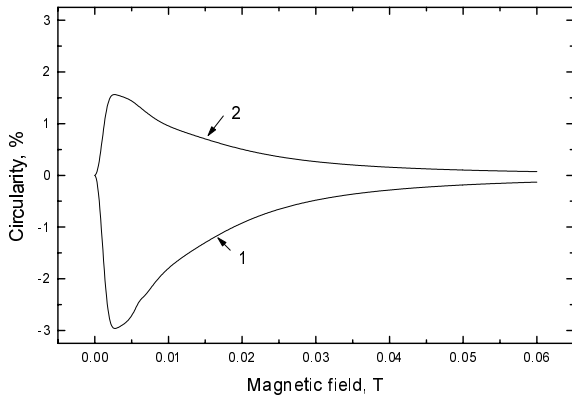
Fig. 2. Fluorescence circularity determined by an orientation of the excited state as dependent on the external magnetic field strength for two types of molecular transitions: $1 - J''_{\text{initial}} = 0 - J' = 1 - J''_{\text{final}} = 0$ and $2 - J''_{\text{initial}} = 0 - J' = 1 - J''_{\text{final}} = 2$.
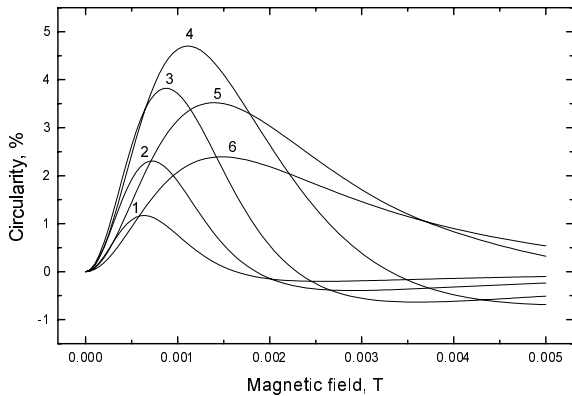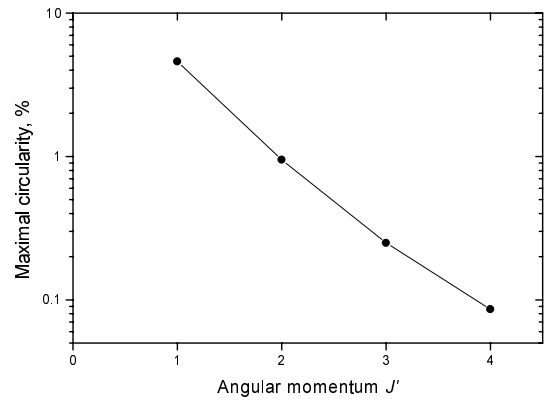

Fig. 3. Fluorescence circularity dependence on magnetic field strength for different values of magnetic hyperfine interaction constant a; $1 - a = 7$ MHz, $2 - a = 10$ MHz, $3 - a = 15$ MHz, $4 - a = 25$ MHz, $5 - a = 50$ MHz, $6 - a = 80$ MHz.

for different molecular transitions in the final stage of an excitation-fluorescence cycle.

As far as, in order to determine different properties of atoms and molecules fluorescence circularity rates are measured that are even smaller than expected due to hyperfine structure, one must be very careful in the analysis of the signals and keep this possible reason for appearance of fluorescence circularity in mind.

On the other hand, this effect can be exploited in itself to determine hyperfine constants of molecules. In order to demonstrate this, let us consider an even more simple situation than the one analyzed above. To make the signal dependent on just one parameter, let as assume that only one nucleus of a molecule has non-zero nuclear spin and that this spin is characterized by a quantum number $I = 1/2$. Then, in the same geometry as considered above for a molecular transition $J''_{\text{initial}} = 0 - J' = 1 - J''_{\text{final}} = 0$, we can calculate the circularity rate as dependent on the magnetic hyperfine constant a (values of Landé factors and relaxation rate are assumed the same as in the previous example). In Figure 3 one can see the signal as dependent on the magnetic hyperfine constant a. This de-

Fig. 4. Maximal fluorescence circularity dependence on the excited state rotational quantum number J'.

pendence is well pronounced and obviously can be used for measurements of a.

An important question is, how the magnitude of the circularity signal is dependent on the excited state angular momentum value. Obviously, the effect must decrease when the excited state angular momentum increases. This follows from a simple model. The total angular momentum F of a molecules is formed by a coupling between the rotational angular momentum J and the nucleus spin angular momentum I. In a magnetic field this coupling breaks down and the total angular momentum F ceases to exist as a good quantity. Instead the rotational angular momentum J starts playing the dominant role. If J, F and I are of the same magnitude, transition form F to J can considerably influence the signal. This is what we see in the examples above. If, on the contrary, J is considerably larger than I, then the total and rotational angular momenta almost coincide, and transition from F to J influences observable signals only insignificantly. In Figure 4 the maximal circularity amplitude for a transition $J''_{\text{initial}} = J - 1 \rightarrow J' = J \rightarrow J''_{\text{final}} = J - 1$ is depicted as dependent on J. For this calculation the value of a magnetic hyperfine constant is assumed as $a = 25$ MHz. Other parameters are as for Figure 3. We can see that the amplitude of the signal decreases almost exponentially with increase in J. This means that the influence of hyperfine structure on the observed signals can be significant only for very small angular momentum values.

We have considered here a simplified situation when only one nucleus causes HFS of a molecule. In the case when two or more nuclear spins are influencing the magnetic sublevel pattern in a magnetic field and consequently the fluorescence signal, the analysis can be performed as well. For this methods have been developed, see for example [27]. Unfortunately, these calculations are rather laborious.

6 Conclusions

From the discussion above the following conclusions may be drawn. First, when one measures alignment-orientation

conversion in presence of an external magnetic field, one must be very careful in the signal analysis. Besides, the non-linear effects of a type discussed in references [10, 16], for which intramolecular perturbations are responsible, similar appearances in experimentally measured circularity rate can be caused by a hyperfine structure which is present almost in all atoms and molecules. The circularity rate caused by a joint action of an external magnetic field and hyperfine interaction can have an amplitude comparable with, if not larger than some features in fluorescence circularity dependence on the magnetic field strength, as observed in experiment and attributed to a specific intramolecular interaction, see [16]. Of course, as shown above, the last conclusion is relevant only for molecular states with small rotational angular momentum, and this was not the case in the experiment cited above.

On the other hand, alignment-orientation transition can be used for good at certain conditions, in measuring hyperfine interaction constants in molecules as well as in atoms. Despite the fact that in the model analyzed above molecules were used as an example, all description could be applied to atoms as well.

Besides, in this paper some relations between atomic and molecular hyperfine structure constants on the one hand, and between constants a, b_0 and b_2 in molecules on the other, have been discussed. This approach can allow to make estimates of necessary molecular hyperfine interaction constants in the cases when only respective atomic constants are available.

References

1. M. Lombardi, C.R. Acad. Sci. B **265**, 191 (1967).
2. V.N. Rebane, Opt. Spectrosc. USSR **51**, 163 (1968).
3. M. Lombardi, in *Beam Foil Spectroscopy*, edited by I.A. Sellin, D.J. Pegg (Plenum Press, New York, 1976), Vol. 2, p. 731.
4. T. Manabe, T. Yabuzaki, T. Ogawa, Phys. Rev. Lett. **46**, 637 (1981).
5. M. Lombardi, J. Phys. France **30**, 631 (1969).
6. M. Auzinsh, R. Ferber, J. Chem. Phys. **99**, 5742 (1993).
7. M. Auzinsh, R. Ferber, *Optical Polarization of Molecules* (Cambridge University Press, Cambridge UK, 1995).
8. M. Auzinsh, Can. J. Phys. **75**, 853 (1997).
9. M. Auzinsh, R. Ferber, Phys. Rev. Lett. **69**, 3463 (1992).
10. O. Nikolayeva, M. Auzinsh, M. Tamanis, R. Ferber, J. Mol. Spectr. **480–481**, 283 (1999).
11. J.C. Lehmann, J. Phys. France **25**, 809 (1964).
12. J.C. Lehmann, Phys. Rev. **178**, 153 (1969).
13. M. Broyer, J. Vigué, J.-C. Lehmann, Chem. Phys. Lett. **22**, 313 (1973).
14. J. Vigué, M. Broyer, J.-C. Lehmann, J. Phys. B **7**, L158 (1974).
15. J. Vigué, M. Broyer, J.-C. Lehmann, J. Chem. Phys. **62**, 4941 (1975).
16. I. Klintsare, M. Tamanis, A.V. Stolyarov, M. Auzinsh, R. Ferber, J. Chem. Phys. **99**, 5748 (1993).
17. M. Auzinsh, A.V. Stolyarov, M. Tamanis, R. Ferber, J. Chem. Phys. **105**, 37 (1996).
18. M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, A.V.Stolyarov, R. Ferber, J. Chem. Phys. **106**, 2195 (1997).
19. I.I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer–Verlag, Berlin, 1979).
20. D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
21. M.-A. Melieres-Marechal, M. Lombardi, J. Chem. Phys. **61**, 2600 (1974).
22. K.F. Freed, J. Chem. Phys. **45**, 4214 (1966).
23. J. Bulthuis, J.M. Milan, H.M. Jassen, S. Stolte, J. Chem. Phys. **94**, 1781 (1991).
24. M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolajeva, R. Ferbers, E.A. Pazyuk, A.V. Stolyarov, A. Zaitsevskii, Phys. Rev. A **58**, 1932 (1998).
25. E. Arimondo, M. Inguscio, P. Violino, Rev. Mod. Phys. **49**, 31 (1977).
26. G. Herzberg, *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules* (D. van Nostrand Company, Princeton, New Yersey, Toronto, London, 1957).
27. C.H. Townes, A.L. Schawlow, *Microwave Spectroscopy* (Dover Pubns, Dover, 1975).
28. W.J. Stevens, D.D. Konowalow, L.B. Ratcliff, J. Chem. Phys. **80**, 1215 (1984).
29. P. Raghavan, A. Data Nucl. Data Tables **42**, 189 (1989)
30. J. Pfaff, M. Stock, D. Zevgolis, Chem. Phys. Lett. **65**, 310 (1979)