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Emergence of circularity at linear polarized excitation of molecules

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General conditions causing partial transformation of optical alignment of excited state angular momenta J into orientation at weak linear polarized broad line excitation of molecules are examined. As is shown, the phenomenon takes place under the effect of an external perturbing factor leading to such magnetic sublevel M splitting $\omega_{MM'}$ when $\omega_{MM\pm 1} \neq \omega_{-M\mp 1-M}$ and $\omega_{MM'}$ is of the order of molecular state relaxation rate. An analytical expression is obtained describing the appearing circularity of fluorescence for arbitrary J values. A numeric example is given for $^1\Sigma$ state molecules with $J=10$ assuming a quadratic Stark effect in a homogeneous external electric field.

I. INTRODUCTION

Excitation of an ensemble of particles (atoms, molecules) with a directed light beam is known to produce anisotropic angular momenta distribution possessing cylindrical symmetry around a certain axis (z axis). If there exists such a plane perpendicular to the z axis that the momenta distribution remains unchanged at reflection in this plane, we have alignment of angular momenta of the ensemble. If the distribution is changed at such a reflection, the angular momenta system possesses orientation. Alignment can be readily illustrated by a double pointed arrow (\leftrightarrow), symbolizing that no singled out direction is created, and the averaged angular momentum value is zero along with the corresponding magnetic moment. Orientation can be denoted as a single pointed arrow (\rightarrow), thus pointing out the preferable direction of momenta distribution. If orientation exists, it leads to a nonzero averaged angular (and magnetic) momentum value. As is clear from symmetry considerations, excitation with a linear polarized light beam is able to create only alignment, the light vector \hat{E} defining the axis of cylindrical symmetry.

It has been of interest for a rather long time to examine perturbing factors able to break this strong symmetry rule and thus to transfer alignment into orientation. The basis of a very fruitful theoretical approach was actually formulated by Fano¹ in 1964. He expanded over irreducible tensorial sets not only the state density matrix but also that of the external perturbation Hamiltonian as well, thus employing the advantages of treatment in terms of polarization moments accounting in a most adequate way for the symmetry properties of the angular momentum distribution. In the case, when we have external perturbation, the z axis of quantization is directed along this perturbation. Let us remind the reader that polarization moments f_Q^k of rank $K=2$ describe alignment (longitudinal for $Q=0$, transversal for $Q=\pm 1, \pm 2$). If only alignment components with $Q=\pm 2$ differ from zero the transversal alignment is perpendicular to the z axis, but if $Q=\pm 1$ components differ from zero the alignment is "tilted" with respect to the z axis.² The moments f_0^1 and $f_{\pm 1}^1$ describe the longitudinal and transversal orientation, respectively. Under certain conditions the tilted alignment components $f_{\pm 1}^2$ can be

transformed into transversal orientation $f_{\pm 1}^1$. There are two groups of works considering this effect: as a result of either anisotropic collisions, or of external field action.

References 3 and 4 have shown that partial alignment-orientation conversion is induced in an atomic ensemble by anisotropic collisions, when the angle between collision axis and that of alignment differs from 0 or $\pm\pi/2$. The idea was later confirmed in experimental observations.^{5,6} Thus in Ref. 6 the anisotropic velocity distribution of excited atoms $\text{Ne}^*(^3P_2)$ was achieved by frequency shifted linear polarized laser excitation. The application of a constant magnetic field $\mathbf{H} \perp \hat{E}$ inclined the axis of optical alignment, thus causing the appearance of tilted alignment ($f_{\pm 1}^2$) components. In this case anisotropic $\text{Ne}^* + \text{Ne}$ collisions are able to transform $f_{\pm 1}^2$ into transversal orientation $f_{\pm 1}^1$. The effect has been detected as an appearance of circularity in fluorescence in agreement with the prediction in Ref. 7 and with detailed description in Ref. 8. A more subtle experiment was performed by Chaika and co-workers.⁹ They used "hidden" alignment in Ne discharge to align $\text{Ne } ^3P_1$ atoms. The axis of this alignment coincides with the symmetry axis of anisotropic collisions. Again, the alignment axis was turned in a weak magnetic field \mathbf{H} , thus leading to a collision induced partial transformation from hidden alignment into orientation. The effect was monitored⁹ via intensity changes with H of a linear polarized probe laser beam passing in \mathbf{H} direction through the discharge tube placed between crossed polarizers. The appearance of orientation causes the appearance of transmitted laser light due to rotation of its \hat{E} vector. The collisional alignment-orientation transformation is, in principle, expected for various kinds of collisions including ion-surface collisions.¹⁰

The other group of works deals with electric field effects. Lombardi¹¹ describes a circularity signal from $\text{He}(4^1D_2)$ in a HF capacitive electrodeless helium discharge. Collisions with electrons served as a source of alignment, whilst external magnetic field \mathbf{H} inclines the produced alignment. The electric field \mathcal{E} of the discharge was considered as a perturbing factor able to produce an orientation signal. Reference 12 observed a circularity signal in fluorescence under linear polarized laser excitation of Ar^+ in a hollow-cathode discharge, applying both elec-

tric and weak magnetic field. The signal was, however, interpreted rather as an effect on tilted alignment of collisions with electrons than as electric field effect. We recently proposed¹³ to apply an external electric field \mathcal{E} directed at angle $\theta = \pi/4$ to the molecular beam direction, in order to convert a distribution of molecules moving with the same velocity \mathbf{v} from having alignment of its \mathbf{J} vectors into one having orientation via second order Stark effect. Estimates performed for a NaK molecule show the possibility to produce rotational and isotope selective \mathbf{J} orientation at impressively small \mathcal{E} values; thus $\mathcal{E} \cong 135 \text{ V cm}^{-1}$ for $J=10$.

The \mathbf{E} -vector action of sufficiently intensive light may be also considered as a source of Stark effect. A demonstration of this effect was made by Cohen-Tannoudji and Dupont-Roc¹⁴ for the case of optically pumped ^{201}Hg atoms. They used the dynamic Stark effect caused by off-resonant strong light beam in order to induce orientation of atoms which were optically aligned by means of a resonant pumping light; the alignment-orientation conversion was of maximal value when the angle between two light vectors was equal to $\pi/4$.

In an optical pumping cycle the common action of dynamic Stark effect and external magnetic field when $\mathbf{H}, \mathbf{E} \neq 0$, $\pi/2$ may also cause alignment-orientation transfer. The calculations for stimulated $0 \leftrightarrow 1$ transitions between $J=0$ and 1 were performed in Ref. 15, and for arbitrary J values in Ref. 16. The similar alignment-orientation transfer effect in case of "depopulation" optical pumping of ground state molecules was calculated in Refs. 17 and 18, the effect being pronounced nonlinear ($f_{\pm 1}^1$ proportional to cubed pumping light intensity) and of pure quantum origin, that is, it disappears at $J \rightarrow \infty$.

The more trivial effect of appearance of longitudinal orientation f_0^1 due to population difference between magnetic sublevels $\pm M$ caused by detuned monochromatic excitation and magnetic field action was treated in Refs. 15 and 19. The case when f_0^1 appears at broad line excitation in magnetic field $\mathbf{H} \perp \hat{\mathbf{E}}$ due to hyperfine decoupling was considered in Refs. 20 and 21 where optical pumping of Rb atoms was examined.

An interesting possibility to produce the orientation of angular momenta of beam molecules was demonstrated by Zare and co-workers.^{22,23} They measured the orientation produced in direct inelastic scattering of N_2 molecules from a single-crystal surface of $\text{Ag}(111)$. The orientation appeared along a direction perpendicular to the scattering plane and was interpreted qualitatively by hard-cube hard-ellipsoid model as a result of the action of the tangential frictional forces.

Finally it is worth mentioning that parity violation is also able to cause fluorescence circularity, and this effect has been predicted²⁴ for some cases, such as $^2\Sigma$ states in $\text{LaO} \cdots \text{LuO}$, to be 10^4 times larger than in the $2s$ state of a hydrogen atom. Such a magnitude of the effect is expected owing to a very small interval between the rotational levels of opposite parity.

As follows from the cited papers, the essential requirement for appearance of transversal orientation $f_{\pm 1}^1$ under linear polarized broad line excitation is an oblique angle

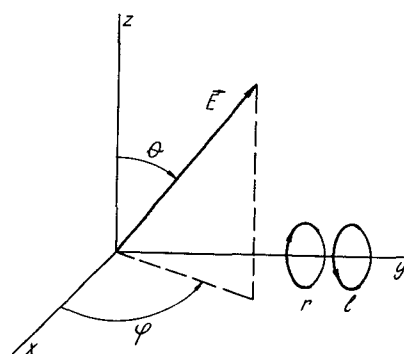


FIG. 1. Excitation and observation geometry.

between alignment axis and that of the external perturbing factor. This requirement is, however, insufficient, as is well known, that, say, orientation does not appear as a result of a linear Zeeman effect at any angle between $\hat{\mathbf{E}}$ and \mathbf{H} . The present paper is aimed at clarifying the general conditions in which the optical alignment of molecules by weak linear polarized broad line excitation can be transformed into orientation under perturbation effect which causes magnetic sublevel splitting $\omega_{MM'}$, and to present an analytical expression for the appearing circularity of fluorescence at arbitrary J values. Since appearing of fluorescence circularity can be detected with extremely high accuracy, the phenomenon promises to serve as an essentially new sensitive method for detailed investigation of intramolecular interactions causing nonlinearity of magnetic sublevel splitting in external fields. One example, which demonstrates such a possibility, is realized in the following paper, cf. Ref. 25, where the experiment on a $\text{Te}_2(A1_u^-)$ molecule was performed showing alignment-orientation conversion due to quadratic Zeeman effect, appearing as a result of magnetic field-induced $\Delta J = \pm 1$ interaction between different electronic states.

II. THEORY

Let us assume that the ensemble of molecules undergoes resonance excitation by a linear polarized light beam with its $\hat{\mathbf{E}}$ vector characterized by the spherical angles θ, φ , cf. Fig. 1. The excitation process creates the excited state (J') density matrix $f_{MM'}$, M, M' being the magnetic quantum numbers. f_{MM} describes the M -level population whilst $f_{MM'}$ describes the coherence between the M, M' levels. The connection between $f_{MM'}$ and polarization moments f_Q^K is^{26,27}

$$f_Q^K = \sum_{MM'} C_{J'MKQ}^{J'M'} f_{MM'}, \quad Q = M' - M, \quad (1)$$

where $C_{J'MKQ}^{J'M'}$ are Clebsch-Gordan coefficients and the projection Q varies between $-K$ and K . In the geometry of Fig. 1 the tilted alignment $f_{\pm 1}^2$ is created. As follows from Eq. (1), $f_{\pm 1}^2$ are formed from the same matrix elements $f_{MM'}$ with $\Delta M = M - M' = \pm 1$ as the orientation components $f_{\pm 1}^1$. However, owing to the symmetry of Clebsch-Gordan coefficients, $f_{\pm 1}^1$ possess zero values. Let us now

see whether the situation will change when molecules are subjected to external perturbation causing magnetic sublevel splitting $\omega_{MM'} = (E_M - E_{M'})/\hbar$. For this purpose we shall analyze the respective density matrix $f_{MM'}$ evolution, assuming that the perturbation does not affect population f_{MM} , and then come back to Eq. (1). In case of stationary $J'' \rightarrow J'$ excitation with a sufficiently broad spectral line the density matrix elements $f_{MM'}$ can be found as a stationary ($\dot{f}_{MM'} = 0$) solution of the kinetic equation,²⁸ namely,

$$f_{MM'} = \frac{\tilde{\Gamma}_p}{\Gamma + i\omega_{MM'}} \sum_{\mu} \langle M | \hat{\mathbf{E}}^* \hat{\mathbf{D}} | \mu \rangle \langle M' | \hat{\mathbf{E}} \hat{\mathbf{D}} | \mu \rangle^*, \quad (2)$$

where μ stands for the ground (lower) state J'' magnetic quantum number, $\hat{\mathbf{D}}$ is the unit vector of an electric transition dipole moment, $\tilde{\Gamma}_p$ is the reduced excitation (pumping) rate which is proportional to exciting light intensity, Γ is the excited state decay rate. The explicit form of dipole transition matrix elements can be found by applying the definition of scalar multiplication in cyclic coordinates E^q, D^q

$$\langle M | \hat{\mathbf{E}}^* \hat{\mathbf{D}} | \mu \rangle = \sum_q (E^q)^* \langle M | D^q | \mu \rangle, \quad (3)$$

and by the Wigner-Eckart theorem^{29,30}

$$\langle M | D^q | \mu \rangle = \frac{1}{\sqrt{2J'+1}} C_{J''M\mu 1q}^{J'M} (J' \| D \| J''), \quad (4)$$

where $(J' \| D \| J'')$ is the reduced matrix element. Putting Eq. (4) into Eq. (3) and then into Eq. (2), we get the $f_{MM'}$ expression in the form:

$$f_{MM'} = \frac{\tilde{\Gamma}_p}{2J'+1} \frac{|(J' \| D \| J'')|^2}{\Gamma + i\omega_{MM'}} \times \sum_{\mu_1 \mu_2} (E^{q_1})^* (E^{q_2}) C_{J''M\mu_1 1q_1}^{J'M} C_{J''M'\mu_2 1q_2}^{J'M'}. \quad (5)$$

Here the first product $\tilde{\Gamma}_p |(J' \| D \| J'')|^2 / (2J'+1) = \Gamma_p$ is often called the pumping rate and will not be discussed in more detail. The second factor, $(\Gamma + i\omega_{MM'})^{-1}$, accounts for external field effect, whilst the sum describes the angular part (geometric factor) of the excitation process. We would like to remind the θ, φ dependence of the cyclic components of vector $\hat{\mathbf{E}}$,

$$\begin{aligned} E^{+1} &= -\frac{1}{\sqrt{2}} (\sin \theta) e^{-i\varphi}, \\ E^0 &= \cos \theta, \\ E^{-1} &= \frac{1}{\sqrt{2}} (\sin \theta) e^{i\varphi}. \end{aligned} \quad (6)$$

The scheme presented in Fig. 2 is aimed at helping to imagine the way of creation nonzero $f_{MM'}$ values following from the symmetry properties of Clebsch-Gordan coefficients. $f_{MM'}$ expressions thus obtained are then introduced into Eq. (1) in order to conclude what polarization moments have been produced. If $\theta=0$, only f_{MM} components differ from zero, yielding according to Eq. (1) only popu-

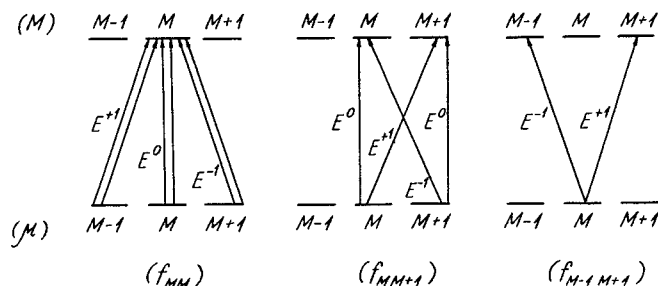


FIG. 2. Scheme of $f_{MM'}$ formation in $\mu \rightarrow M$ transitions induced by linear polarized light.

lation f_0^0 and longitudinal ($Q=0$) alignment f_2^0 . If $\theta = \pi/2$, matrix elements f_{MM} and $f_{M \mp 1 M \pm 1}$ arise, producing not only f_0^0 and f_2^0 , but the transversal ($Q = \pm 2$) alignment $f_{\pm 2}^2$ as well. It is important to point out that orientation f_1^0 does not appear in these cases. As may be seen, if θ differs from zero and $\pi/2$, the components f_{MM} , $f_{MM \pm 1}$, and $f_{M \mp 1 M \pm 1}$ appear, leading to polarization moments f_0^0 , f_1^0 , $f_{\pm 1}^1$, and $f_{\pm 2}^2$. The fact that the transversal orientation $f_{\pm 1}^1$ is not produced can be understood, taking into account that $f_{MM \pm 1} = -f_{-M \mp 1 -M}$, and

$$\begin{aligned} f_{\pm 1}^1 &= \sum_{MM'} C_{J'M \pm 1}^{J'M'} f_{MM'} \\ &= \sum_M C_{J'M \pm 1}^{J'M \pm 1} f_{MM \pm 1} \\ &= \mp \sum_M \sqrt{\frac{(J' \pm M \pm 1)(J' \mp M \mp 1 + 1)}{2J'(J' + 1)}} f_{MM \pm 1}. \end{aligned} \quad (7)$$

Hence $f_{MM \pm 1}$ and $f_{-M \mp 1 -M}$ are entering the sum of Eq. (1) for $f_{\pm 1}^1$ with equal coefficients, thus resulting in $f_{\pm 1}^1 = 0$. This, in fact, also explains why external field effect is not able to produce orientation when E_M is proportional to the field strength: $E_M \propto M \times \text{external field strength}$, thus leading to $\omega_{MM'} \propto (M - M') \times \text{external field strength}$ and $\omega_{MM \pm 1} = \omega_{-M \mp 1 -M}$. In case of such external field action the equality $f_{MM \pm 1} = -f_{-M \mp 1 -M}$ is still valid and $f_{\pm 1}^1$ remains zero.

Let us now assume that external perturbation is removing degeneration between M, M' sublevels in such an "asymmetric" way, that

$$\omega_{MM \pm 1} \neq \omega_{-M \mp 1 -M}. \quad (8)$$

This leads to $f_{MM \pm 1} \neq -f_{-M \mp 1 -M}$ and thus results in arising excited state transversal orientation, $f_{\pm 1}^1 \neq 0$. The last contention may be formulated in a more general way. We may introduce the multipole moments ω_0^X of a perturbation, cf. Ref. 1,

$$\omega_0^X = \sum_M C_{J'MX0}^{J'M} \omega_M, \quad \omega_M = E_M/\hbar, \quad (9)$$

where E_M is the energy shift of the M sublevel due to perturbation. If even rank X components of ω_0^X differ from zero (as it is in cases of quadratic Stark or Zeeman effects), alignment-orientation conversion will take place. If only odd rank components differ from zero (as it is in the case

of linear Zeeman effect), such conversion is impossible. Conditions (8) and (9) are the only way in which an external field is able to produce transformation from alignment into orientation. Indeed, the perturbation is neither able to affect light polarization (E^q), nor, of course, the Clebsch–Gordan coefficients determining the angular factor in Eq. (5). The pumping rate Γ_p remains constant, as we suppose that energetic conditions of excitation remain unchanged in an external field in case of broad exciting line approximation. We also neglect the effect of any anisotropic “pure” depolarizing collisions, thus assuming a relaxation rate Γ independent of M, M' .

The prerequisite for creation of orientation in aligned state can be restated in terms of time reversal properties of a Hamiltonian operator which represents the perturbation. The conclusion is that alignment–orientation conversion will take place only if the time invariant Hamiltonian is involved.³¹ For instance, the Hamiltonian operator of linear Zeeman effect is odd under time reversal¹¹ and thus is not able to cause the conversion. On the contrary, the Hamiltonian operator of quadratic Stark effect is even under time reversal and, as a consequence, the quadratic Stark effect can produce alignment–orientation conversion.

We shall further discuss the manifestation of transversal orientation $f_{\pm 1}^1$ in $J' \rightarrow J''$ fluorescence. The general expression for fluorescence intensity I_f in terms of density matrix $f_{MM'}$ can be written in the form²⁸

$$I_f = K \sum_{\mu MM'} f_{MM'} \langle \mu | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | M \rangle \langle \mu | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | M' \rangle^*, \quad (10)$$

where $\hat{\mathbf{E}}_f$ is the unit polarization vector of emitted light. Applying similar manipulations as employed above in passing from Eq. (2) to Eq. (5), we get an explicit form of Eq. (10)

$$I_f = \frac{K | \langle J'' || D || J' \rangle |^2}{2J' + 1} \sum_{\mu MM' q_1 q_2} f_{MM'} \times (-1)^{q_1 + q_2} (E_f^{-q_1})^* E_f^{-q_2} C_{J'' \mu 1 q_1}^{J' M} C_{J'' \mu 1 q_2}^{J' M'}, \quad (11)$$

where $E_f^{q_i}$ are cyclic components of $\hat{\mathbf{E}}_f$.

It is most straightforward to certify the creation of excited state orientation by way of appearance of fluorescence circularity, namely, the nonzero difference $I_r - I_l$, where I_r, I_l are right-handed and left-handed circularly polarized light intensities. It is often convenient to measure the normalized quantity, namely the degree of circularity

$$\mathcal{C} = \frac{I_r - I_l}{I_r + I_l}. \quad (12)$$

If light emission is viewed along the z axis, only $E_f^{-1} = 1$ differs from zero for I_l and $E_f^1 = 1$ for I_r . As, however, only the transversal orientation $f_{\pm 1}^1$ has been produced in our case, we can not expect to obtain $\mathcal{C} \neq 0$, if fluorescence light is spreading along the quantization axis.² Let us thus choose the y axis as observation direction, cf. Fig. 1. This means that the cyclic components E_f^q entering into Eq. (11) are to be transformed by means of Wigner D matrices^{29,30}

$$E_f^q = \sum_{q'} E_f^{q'} D_{q'q}^{(1)*}(\alpha, \beta, \gamma), \quad (13)$$

where α, β, γ are Euler angles describing the turn of the coordinate system in Fig. 1 to one with a “new” z' axis directed along the “old” y axis. Accounting for this and combining Eqs. (5) and (11), the following final expressions can be found:

$$I_r - I_l \propto \Gamma_p \frac{\sin 2\theta}{2} \sum_M \frac{\Gamma \sin \varphi + \omega_{MM+1} \cos \varphi}{\Gamma^2 + \omega_{MM+1}^2} (C_{J'' M+11-1}^{J' M} C_{J'' M+110}^{J' M+1} - C_{J'' M10}^{J' M} C_{J'' M11}^{J' M+1}) (C_{J'' M10}^{J' M} C_{J'' M+11}^{J' M+1} + C_{J'' M+11-1}^{J' M} C_{J'' M+110}^{J' M+1}), \quad (14)$$

$$I_r + I_l \propto \sum_M \frac{\Gamma_p}{\Gamma} \left[\frac{\sin^2 \theta}{2} [(C_{J'' M-111}^{J' M})^2 + (C_{J'' M+11-1}^{J' M})^2] + \cos^2 \theta (C_{J'' M10}^{J' M})^2 \right] \left[\frac{1}{2} (C_{J'' M-111}^{J' M})^2 + (C_{J'' M10}^{J' M})^2 + \frac{1}{2} (C_{J'' M+11-1}^{J' M})^2 \right] + \Gamma_p \frac{\sin^2 \theta}{2} \frac{\Gamma \cos 2\varphi - \omega_{M-1M+1} \sin 2\varphi}{\Gamma^2 + \omega_{M-1M+1}^2} C_{J'' M-1-1}^{J' M-1} C_{J'' M+11}^{J' M+1} C_{J'' M-1-1}^{J' M-1} C_{J'' M+11}^{J' M+1}, \quad (15)$$

allowing to compute the orientation signal, $I_r - I_l$ or the degree of circular polarization of fluorescence, \mathcal{C} , cf. Eq. (12) and Fig. 1, excited by a linear polarized light beam with arbitrary direction of $\hat{\mathbf{E}}(\theta, \varphi)$. Note, that knowledge of $\omega_{MM'}$, namely, of the magnetic sublevel energy set E_M , is the only information about perturbation needed to compute the signal.

III. AN EXAMPLE: QUADRATIC STARK EFFECT

Let us consider the situation when an external homogeneous electric field \mathcal{E} is applied along the z axis, Fig. 1. We will use quadratic Stark effect energy expression in form³²

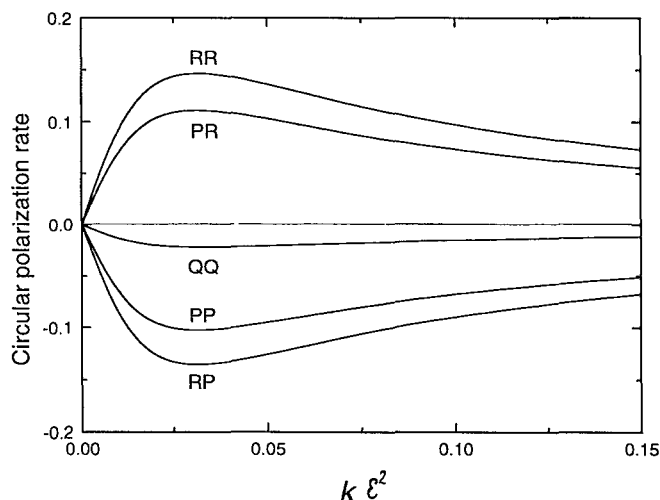


FIG. 3. Calculated degree of circularity under linear polarized excitation as dependent on squared electric field \mathcal{E}^2 for different absorption-fluorescence branches.

$$E_M = \frac{d^2 \mathcal{E}^2}{hB} \left[\frac{J(J+1) - 3M^2}{2J(J+1)(2J-1)(2J+3)} \right], \quad (16)$$

d being the electric dipole moment, B —the rotational constant of a rigid rotator. As can be seen from Eq. (14), $\theta_0 = 45^\circ$ is an optimal angle between \mathcal{E} and \hat{E} to obtain maximal circularity of fluorescence viewed along the y axis, cf. Fig. 1. The choice of azimuth angle φ value needs more discussion. First, one must remember that the $I_r - I_l$ signal appears only if the longitudinal orientation component along the observation direction possesses nonzero value. In the case, when E_M is given by Eq. (16), orientation appears only in the direction perpendicular to the \mathcal{E} , \hat{E} plane, hence φ thus must differ from $\pi/2$ possessing the optimal value $\varphi = 0$. This can be seen from the form of the φ dependence in Eq. (14). Indeed, as E_M is dependent only on M^2 , cf. Eq. (16), we have $\omega_{MM+1} = -\omega_{-M-1-M}$. The circularity $I_r - I_l$ is zero for $\varphi = \pi/2$ since the terms in Eq. (14) contain ω_{MM+1}^2 only, whilst the total product of Clebsch-Gordan coefficients change the sign when we pass from $M, M+1$ term to $-M-1, -M$ term. In fact, this might be a sensitive test to check type of Stark effect for a certain molecular state.

In the special case $J'' = J'_1 = 0$, $J' = 1$, the analytic solution of Eqs. (14)–(16) for $\varphi = 0$ may be obtained, leading to a simple formula

$$\mathcal{C} = \frac{I_r - I_l}{I_r + I_l} = \frac{(\omega_{01}/\Gamma)}{1 + (\omega_{01}/\Gamma)^2}. \quad (17)$$

A result of numeric computation for $J=10$ is presented in Fig. 3. The degree of circularity \mathcal{C} is given as dependent on a dimensionless parameter $k\mathcal{E}^2$, where

$$k = \frac{d^2}{hB\Gamma} \frac{1}{2J(J+1)(2J-1)(2J+3)},$$

for all types (P, Q, R) of molecular transitions in excitation and radiation processes. The signal possesses maximal

value in the region $\omega_{MM'} \sim \Gamma$, dropping to zero when $\omega_{MM'} \gg \Gamma$, that is when the M, M' coherence is completely destroyed. As the creation of transversal orientation $f_{\pm 1}^1$ by perturbation leading to E_M in form of Eq. (16) is independent of the type of molecular transition in excitation, the signals caused by the different absorption branches (P or R) have the same signs for the same radiation branches. It is easy to understand³³ that the difference between, say, PR and RR will vanish with $J \rightarrow \infty$. It is also clear, cf. Ref. 33, that the degree of circularity for a QQ type of transition must tend to zero with J .

To consider a concrete electric field scale, let us take NaK as an example of a diatomic molecule possessing a relatively large electric dipole moment value. For example, taking for the $C(3)^1\Sigma^+$ state the values $d = 2.7$ D,³⁴ $B = 0.0905$ cm⁻¹ (Ref. 35) and assuming the inverse spontaneous decay time $\tau^{-1} = \Gamma = 10^8$ s⁻¹, we get

$$k \approx \frac{4.6 \times 10^{-5}}{2J'(J'+1)(2J'-1)(2J'+3)}.$$

Hence, an electric field $\mathcal{E}_{\max} \approx 400$ V/cm is needed to obtain signal maxima for $J=1$, and $\mathcal{E}_{\max} \approx 8.5$ kV/cm for $J=10$, Fig. 3. \mathcal{E}_{\max} value is growing rapidly with J , reaching $\mathcal{E}_{\max} \approx 250$ kV/cm for $J=100$.

IV. CONCLUDING REMARKS

The nonequidistant splitting of magnetic sublevels by perturbation effect, when the requirements of Eqs. (8) and (9) are fulfilled, is able to produce partial conversion of the excited state alignment induced by weak linear polarized optical excitation into the transversal orientation of the excited molecular level. The orientation manifests itself in appearing fluorescence circularity. One of the simplest examples is the effect of a homogeneous electric field, causing the quadratic Stark effect and leading to a considerably high degree of circularity for R, P types of molecular transitions, varying from $\mathcal{C} = 0.5$ for $J=1$ to $\mathcal{C} \approx 0.12$ for $J \rightarrow \infty$. The measurements of appearing circularity can be expected to provide a useful method for the determination of dipole moments and (or) the relaxation rates, for studying the Stark effect origin and the symmetry of an excited state. It is worth noting that the alignment-orientation conversion is expected to appear also in other cases, such as nonlinear Zeeman splitting caused by magnetic field due to simultaneous action of both external and intramolecular interaction. The latter case is considered in a following paper²⁵ where experimental results are presented.

ACKNOWLEDGMENT

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