Orientation of atoms and molecules under excitation by elliptically polarized light

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The fluorescence recording and excitation conditions of atoms or molecules are proposed for the case where the changes in the degree of circular polarization of radiation in an external magnetic field depend solely on the orientation decay rate γ_1. Here a simple Lorentzian or dispersion signal waveform is achieved, i.e., the same type as in the case of the Hanle effect for linearly polarized or unpolarized excitation. These conditions are satisfied with elliptically polarized excitation or observation with given ellipticity parameters and a given light propagation direction. Optimum angles characterizing the experimental geometry are obtained for different angular momenta and transition types. The possibility for applying the proposed experimental scheme to quantum beating of radiation in order to obtain a signal with beating at only a single frequency corresponding to the splitting between the magnetic sublevels with $|\Delta m| = 1$ is considered.

The states of atoms and molecules which are used in conjunction with an external perturbing action to generate coherence are characterized by a set of tensors. These tensors are called the polarization moments (PM).[1,2] The zero-rank PMs characterize the state population, the first-rank tensor is a vector, and its three components characterize the orientation of the average angular momentum of the particle ensemble. The second-rank tensor is called the alignment. The relaxation of polarization moments of various ranks in a number of important practical processes such as radiative decay and isotropic collisional breakdown of the state will occur independently and is characterized by a set of relaxation constants γ_K, where K is the rank of the corresponding tensor.

Polarization moments of rank $K \leqslant 2$ may arise by absorption of weak resonance light from a dipole transition in the excited state.[1] However even if polarization moments of ranks above two are created by some more complex method in the excited state, only PMs with $K < 2$ will have an effect on the intensity or polarization of fluorescence from this state. Hence it is important for atomic and molecular spectroscopy to know the relaxation rates of the rank 0, 1, and 2 PMs. It is not difficult to determine the population relaxation rate γ_0 or the alignment relaxation rate γ_2. Thus γ_0 can be determined directly from the fluorescence decay kinetics after pulsed linearly polarized or unpolarized excitation. The alignment relaxation rate γ_2 can be determined from fluorescence depolarization by an external magnetic field—the Hanle effect.[2]

The situation is more complex in analyzing the orientation relaxation rate γ_1; comparatively few studies have been devoted to this problem, particularly for molecules (see Ref. 3 and the literature cited therein). When atomic and molecular orientations are generated by circularly polarized light alignment always occurs as well, which represents an interfering factor in the experiments (see, for example, Refs. 3–5). It has not yet been possible to isolate a signal but contains only the single relaxation parameter γ_1.

The present paper proposes a method of solving this problem by using elliptically polarized excitation or by observing with given parameters the ellipticity and propagation direction of the light. In measuring magnetic-field breakdown; for example, the degree of circular polarization, the recorded signal waveform will depend solely on γ_1. It is also demonstrated that under these excitation and observation conditions the quantum beating signal[6] in an external magnetic field contains a single frequency corresponding to the splitting of the magnetic sublevels with $|\Delta m| = 1$.

The light polarization e will be characterized by means of a second-rank tensor Φ_Q^K whose components can be given as[1]

$$\Phi_Q^K(\mathbf{e}) = \sum_{q_1 q_2} (-1)^{q_2} e_{q_1} e^*_{q_2} \begin{pmatrix} 1 & 1 & K \\ q_1 & -q_2 & -Q \end{pmatrix}, \qquad (1)$$

where e_q are the angular components of the vector e, while the quantity in braces is the $3j$ symbol.

Initially we assume that excitation is initiated along the z axis (Fig. 1). A linearly polarized light beam whose polarization vector e forms an angle ξ with the x axis is transmitted through a $\lambda/4$ plate whose fast axis $\mathbf{a}_r$ is parallel to the x axis. We obtain elliptically polarized light after the $\lambda/4$ plate; this light is characterized by the tensor Φ_Q^K with components $\Phi_0^0 = -1/\sqrt{3}$, $\Phi_0^1 = (1/\sqrt{6})\sin 2\xi$, $\Phi_{\pm 1}^1 = 0$, $\Phi_0^2 = -1/\sqrt{30}$, $\Phi_{\pm 1}^2 = 0$, $\Phi_{\pm 2}^2 = (1/2\sqrt{5})\cos 2\xi$.

We write the tensor Φ_Q^K for an arbitrary excitation direction which is described by the spherical angles θ and φ and also for a random configuration of the fast axis of the phase plate $\mathbf{a}_r$ which is characterized by the angle α between $\mathbf{a}_r$ and the plane containing the axis z and the excitation ray. Since α, θ, and φ correspond to the Euler angles on rotation of the physical system,[7] the tensor Φ_Q^K in the rotated system is expressed through the components of tensor $\Phi_Q^{K\prime}$ in the initial system as

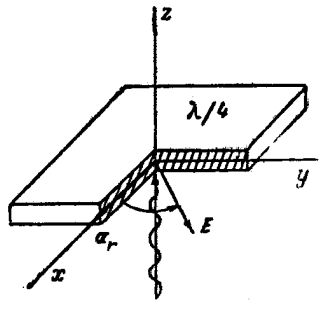

FIG. 1. Scheme for obtaining elliptically polarized light.

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$$\Phi_Q^K = \sum_{Q'} \left(D^K_{QQ'}(\alpha, \theta, \varphi)\right)^* \Phi^K_{Q'}, \qquad (2)$$

or in explicit form

$$\Phi_0^0 = -\frac{1}{\sqrt{3}}; \quad \Phi_0^1 = \frac{1}{\sqrt{6}} \sin 2\xi \cos\theta,$$

$$\Phi_1^1 = -(\Phi_{-1}^1)^* = \frac{1}{2\sqrt{3}} \sin 2\xi \sin\theta e^{i\varphi},$$

$$\Phi_0^2 = \frac{1}{2\sqrt{30}} (3\sin^2\theta \cos 2\alpha \cos 2\xi - 3\cos^2\theta + 1),$$

$$\Phi_1^2 = -(\Phi_{-1}^2)^*$$

$$= -\frac{1}{2\sqrt{5}} [\cos 2\xi \sin\theta (i \sin 2\alpha - \cos 2\alpha \cos\theta) + \sin\theta \cos\theta] e^{i\varphi},$$

$$\Phi_2^2 = (\Phi_{-2}^2)^* = \frac{1}{4\sqrt{5}} [(1 + \cos^2\theta) \cos 2\xi \cos 2\alpha$$

$$+ 2i \cos\theta \cos 2\xi \sin 2\alpha - \sin^2\theta] e^{2i\varphi}. \qquad (3)$$

which follows from the Wigner matrix $D^K_{QQ'}(\alpha,\theta,\varphi)$ (see, for example, Refs. 2 and 7). Equation (3) contain as particular cases the form of the tensor Φ_Q^K for linearly polarized ($\xi = 0,\ \pi/2$) and circularly polarized ($\xi = \pi/4,\ 3\pi/4$) light. When the angle $\xi = \pi/4$ the light is left-circularly polarized, and with $\xi = 3\pi/4$ it is right-circularly polarized.

Under stationary excitation the polarization moments f_Q^K are generated on the upper level; their magnitude can be calculated as Ref. 1

$$f_Q^K = \frac{\mathscr{F}_Q^K}{\gamma_K - iQ\omega}, \qquad (4)$$

where $\mathscr{F}_Q^K$ is the excitation tensor; $\omega = g\mu_B B/\hbar$ is the Zeeman splitting frequency of the excited level in an external magnetic field B along the z axis, g is the Lande factor, μ_B is the Bohr magneton. The excitation tensor $\mathscr{F}_Q^K$ is related to the angular momenta J'', J' of the ground and excited states and the tensor Φ_Q^K decharacterizing the polarization of the excitation light,[1]

$$\mathscr{F}_Q^K = (-1)^{\Delta} \Gamma_p \begin{Bmatrix} 1 & 1 & K \\ J' & J' & J'' \end{Bmatrix} \Phi_Q^K, \qquad (5)$$

where $\Delta = J' - J''$ is the light absorption rate, the figure in braces is the $6j$ symbol. For the molecular states where the angular momenta reach values of several tens and occasionally hundreds, it is possible to pass to the limit $J', J'' \to \infty$ in which[8]

$$\mathscr{F}_Q^K = (-1)^{\Delta} \Gamma_p (2K+1)^{-1/2} \begin{pmatrix} 1 & 1 & K \\ \Delta & -\Delta & 0 \end{pmatrix} \Phi_Q^K. \qquad (6)$$

As demonstrated by a joint analysis of Eqs. (3), (5), and (6), it is impossible to generate conditions to avoid alignment in the excited state, i.e., to assure that all alignment tensor components f_Q^2 are equal to zero. However, if we use elliptically polarized light when

$$\alpha = 0,\ \varphi = 0,\ \cos 2\xi = \sin^2\theta/(1 + \cos^2\theta), \qquad (7)$$

a situation occurs when $\Phi^2_{\pm 2} = 0$ and, consequently, no alignment components $f^2_{\pm 2}$ are created. At the same time a transverse orientation is generated on the excited level, since $f^1_{\pm 1} \neq 0$.

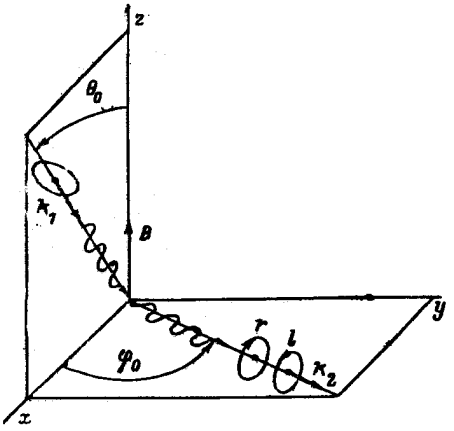

FIG. 2. Scheme for elliptically polarized excitation and recording of the degree of fluorescence circular polarization; the wave vector $\mathbf{k}_1$ lies in the xz plane, the wave vector $\mathbf{k}_2$ lies in the xy plane.

If under these conditions we now record the changes in the degree of circular polarization of fluorescence in an external magnetic field (Fig. 2) the signal will unambiguously be determined by the magnetic-field-induced breakdown of transverse orientation. Using the light intensity formula for the fluorescence of the transition whose final state has the angular moment J_1'' (see Refs. 1 and 2)

$$I \sim (-1)^{\Delta'} \sum_K (2K+1) \begin{Bmatrix} 1 & 1 & K \\ J' & J' & J_1'' \end{Bmatrix} \sum_Q (-1)^Q f_Q^K \Phi^K_{-Q}, \qquad (8)$$

where $\Delta' = J' - J_1''$, while Φ_Q^K characterizes the fluorescence light polarization, detected by the recorder. Assume a detector in the xy plane is used for recording and the direction to the detector is characterized by the angle φ_0. Then the degree of circular polarization can be given as

$$C = \frac{I_r - I_l}{I_r + I_l} = \frac{(-1)^{\Delta'} 2\sqrt{3} \begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J_1'' \end{Bmatrix} (\mathrm{Re}\, f_1^1 \cos\varphi_0 + \mathrm{Im}\, f_1^1 \sin\varphi_0)}{\frac{2}{3\sqrt{2J''-1}} f_0^0 + (-1)^{\Delta'} \frac{5}{\sqrt{30}} \begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J_1'' \end{Bmatrix} f_0^2}, \qquad (9)$$

where I_r and I_l are the right- or left-circularly polarized components of emission intensity. In this expression only $\mathrm{Re}\, f_1^1$ and $\mathrm{Im}\, f_1^1$ will be dependent on the magnetic field. It is possible to find the value of the polarization moments entering into Eq. (10) using Eqs. (4) and (5)

$$\mathrm{Im}\, f_1^1 = (-1)^{\Delta} \frac{\Gamma_p \omega}{\gamma_1^2 + \omega^2} \frac{(2J'+1)^{3/2}}{(2J''+1)} \begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J'' \end{Bmatrix} \Phi_0^1 n_{J''},$$

$$\mathrm{Re}\, f_1^1 = (-1)^{\Delta} \frac{\gamma_1 \Gamma_p}{\gamma_1^2 + \omega^2} \frac{(2J'+1)^{3/2}}{(2J''+1)} \times \begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J'' \end{Bmatrix} \Phi_0^1 n_{J''}, \quad f_0^0 = \frac{\Gamma_p}{\gamma_0} \frac{1}{3} \frac{2J'+1}{2J''+1} n_{J''},$$

$$f_0^2 = (-1)^{\Delta} \frac{\Gamma_p}{\gamma_2} \frac{(2J'+1)^{3/2}}{(2J''+1)} \begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix} \Phi_0^2 n_{J''}, \qquad (10)$$

where $n_{J''}$ is the population of the lower level J'' from which the optical population of the test level J' occurs. The wave-

form of the signal $C(\omega)$ will depend on the observation direction. For observation along the x axis when $\varphi_0 = 0$

$$C(\omega) = A\frac{\gamma_1}{\gamma_1^2+\omega^2}. \tag{11a}$$

while for observation along the y axis when $\varphi_0 = \pi/2$,

$$C(\omega) = A\frac{\omega}{\gamma_1^2+\omega^2}. \tag{11b}$$

Equations (11) have a Lorentzian and dispersion form characteristic of traditional Hanle signals[1] and make it possible to easily determine the rate of orientation relaxation γ_1 of interest to us. The signal amplitude A is determined by the specific values of the angles θ and ξ when condition (7) is satisfied, as well as the values of the angular momenta J'', J', and J_1''. We find that the maximum signal amplitude will be achieved when

$$\cos 2\theta = -\frac{1}{3}\left(1-(-1)^{\Delta'}3\frac{\gamma_0}{\gamma_2}(2J'+1)\begin{Bmatrix}1 & 1 & 2\\ J' & J' & J_1''\end{Bmatrix}\begin{Bmatrix}1 & 1 & 2\\ J' & J' & J''\end{Bmatrix}\right)$$

$$= -\frac{1}{3}\left\{1-\frac{\gamma_0}{\gamma_2}\frac{(2J'+1)}{10}\right.$$

$$\left.\times\frac{[3X(X-1)-8J'(J'+1)][3X_1(X_1-1)-8J'(J'+1)]}{(2J'-1)2J'(2J'+1)(2J'+2)(2J'+3)}\right\}, \tag{12}$$

where $X = 2+J'(J'+1)-J''(J''+1)$ and $X_1 = 2+J'(J'+1)-J_1''(J_1''+1)$.

Figure 3 shows the optimum θ for the case $\gamma_0/\gamma_2 = 1$ as a function of J' for various transitions together with the corresponding signal amplitude. In the limit of large angular momenta, i.e., for molecules we obtain $\cos 2\theta = -3/10$ or $\theta \approx 53.73°$, while the signal amplitude is equal to $A = 5/\sqrt{91} \approx 0.5241$.

We can use another experimental scheme in order to simplify the technical implementation: Circularly polarized light can be used for excitation perpendicular to the external magnetic field **B** while the observation occurs at an angle θ to **B**, isolating the two elliptically polarized components corresponding to the two values of $\pm\cos\xi$ obtained by solving Eq. (7). The proposed experimental scheme can produce certain advantages when recording quantum beating after pulsed excitation as well. When the excitation pulse duration is much less than γ_K^{-1} the excited state may give rise to polarization moments whose temporal evolution after cessation of excitation is defined by the expression[8]

$$f_Q^K(t) = {}_0f_Q^K e^{-(\gamma_K - iQ\omega)t}, \tag{13}$$

where ${}_0f_Q^K$ is the polarization moment at the pulse instant. A harmonically modulated signal at a single modulation frequency ω may be observed for the case of excitation by elliptically polarized light in the previously examined geometry and for observation perpendicular to the magnetic field. Such an experiment makes it possible to determine the Landé factor of the excited state. For example for molecular transitions with a large angular momentum at angles $\alpha = 0$, $\varphi = 0$ characterizing the excitation light the value of θ is arbitrary [while observing condition (7)], while for observation in the direction $\theta_0 = \pi/2$, φ_0 is arbitrary and the expression for I_r takes the form

$$I_r = \frac{\Gamma_p}{\gamma_0}\left[\frac{1}{9}e^{-\gamma_0 t} + \frac{\Gamma_p}{\gamma_2}\frac{1}{90}e^{-\gamma_2 t}\frac{1-2\cos^2\theta}{1+\cos^2\theta}\right.$$

$$\left.\pm\frac{1}{12}\frac{\Gamma_p}{\gamma_1}e^{-\gamma_2 t}\frac{\sin\theta\cos\theta}{1+\cos^2\theta}\cos(\omega t-\varphi_0)\right]. \tag{14}$$

where the sign in front of the last term corresponds to $P\uparrow P\downarrow$ and $R\uparrow R\downarrow$ transitions during the absorption–emission cycle, while the minus corresponds to the $P\uparrow R\downarrow$ and $R\uparrow P\downarrow$ transitions. If we record I_l, the minus sign corresponds to identical transitions in the absorption-emission cycle, while the plus sign corresponds to different transitions.

An analysis of Eq. (14) demonstrates that for $\theta = \pi/4$ the second term corresponding to the decay of alignment at a rate γ_2 drops. Here the ratio of the amplitude of the modulated component to the amplitude of the unmodulated part $\eta = 1/2$ (if we set $\gamma_1 = \gamma_0$, which is a typical value for two-atom molecules[9]). If we select $\cos 2\theta = -8/30$ the modulation percentage is maximized and reaches $5/\sqrt{91} \approx 0.52$, which corresponds to the amplitude of signal (11). Hence such signals have a higher modulation percentage than due the quantum beating signals for the P and R-type transitions under linearly polarized excitation, when η is equal to 1/7.

An analogous calculation can be carried out transitions with an arbitrary angular momentum. The analysis reveals that in this case the largest value of η is achieved at the same angles θ where the highest signal amplitude (11) is achieved (Fig. 3). Here η coincides with the value of A shown in Fig. 3.

The versions examined in the present paper for generating orientation can also be applied to other types of interference phenomena in radiation. Thus, for the quantum beating resonance[6] that occurs when the harmonic modulation frequency of the excitation light overlaps the splitting frequency of the interference sublevels the proposed excitation and observation scheme when condition (7) is satisfied creates a situation where only a single resonance signal (between

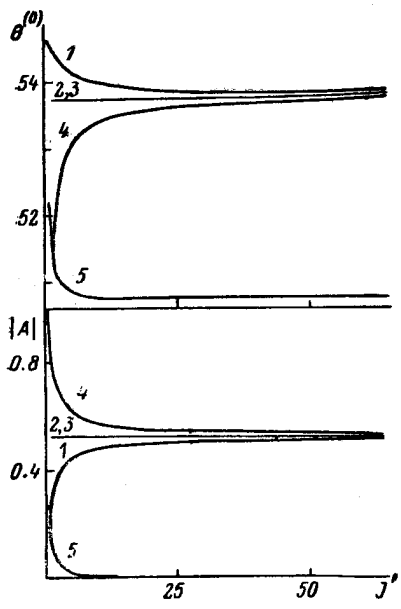

FIG. 3. Optimum angle θ for transitions. *1*—$J''\to J' = J''-1 \to J_1''(P\uparrow P\downarrow)$, *2*—$J''\to J' = J''-1\to J_1'' = J''-2(P\uparrow R\downarrow)$, *3*—$J''\to J' = J''+1\to J_1'' = J''+2(R\uparrow P\downarrow)$, *4*—$J''\to J' = J''+1 \to J_1'' = J''(R\uparrow R\downarrow)$, *5*—$J''\to J' = J''\to J_1'' = J''(Q\uparrow Q\downarrow)$.

$|\Delta m| = 1$) with a width determined by the orientation relaxation rate γ_1 is observed. Here it is occasionally more convenient if the resonance is in a different magnetic field range (or a different modulation frequency range) compared to resonance beating that occurs from the restoration of orientation, i.e., between $|\Delta m| = 2$.

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