

Possibility of experimental observation of the influence of the dynamic Stark effect on the polarization of laser-induced fluorescence of dimers

M. P. Auzinsh

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The results of numerical modeling of the influence of the dynamic Stark effect on the interaction of intense laser radiation with dimers placed in an external magnetic field are presented. It is shown that as a result of the action of the effect being analyzed, under excitation by linearly polarized light, circularly polarized radiation may appear in the fluorescence. The expected degree of circular polarization for real molecules is estimated. The possible influence of the action of the dynamic Stark effect on the degree of linear polarization of laser-induced fluorescence is analyzed.

It is well known that during absorption of linearly polarized light by atoms or molecules, the subsequent fluorescence of these particles is also linearly polarized. However, a number of cases are known in which, in addition to the linearly polarized component of the fluorescence, a component may arise whose degree of circular polarization will be non-zero. In the description of this effect in terms of polarization moments (PM),¹ the effect may be due to the transition of the alignment, produced by linearly polarized light, of the angular momenta of the particles to orientation. Such a transition may be due to different causes. The simplest case involves excitation of atoms placed in a magnetic field directed along the propagation of linearly polarized light not reso-

nant with the absorption frequency of the atoms.² Then the magnetic sublevels of the atom, which differ only in the sign of the magnetic quantum number M , are excited with different efficiencies; orientation of the atoms along the magnetic field arises, i.e., longitudinal orientation, and the fluorescence in this direction is circularly polarized.

Orientation of the atoms across the magnetic field may arise during excitation by linearly polarized resonance light, when an external anisotropic perturbation is superimposed on the ensemble, for example: anisotropic collisions³ or an electric field,^{4,5} both of which are directed at an angle different from 0 and $\pi/2$ to \mathbf{E} , the vector of the exciting light.

Occasionally, this anisotropic factor, which gives rise to

orientation, may be the linearly polarized exciting light itself, or, more accurately, the dynamic Stark effect (DSE) caused by it.⁶

Kotlikov⁷ discussed the influence of DSE on the degree of circularity of laser-induced fluorescence (LIF) for the transition $J'' = 0 \rightarrow J' = 1, \rightarrow J_1'' = 0$, where J'' is the quantum number of the angular momentum of the initial state, J' is that of the excited state, and J_1'' is that of the final state in the absorption-emission cycle for atoms located in an external magnetic field. Finally, Auzinsh⁸ analyzed the influence of DSE on the vibrational-rotational level with angular momentum J'' of the ground electronic state of dimers and the changes in the polarization of LIF caused by this influence. This analysis was made in a model where the spectral profile of the excitation line was much broader than that of the absorption line, but the centers of the two contours did not coincide, giving rise to DSE. The following characteristics of the phenomenon of transition of alignment to orientation were brought out in Ref. 8: (1) The effect in this case is purely a quantum one and disappears in the passage to the classical limit $J \rightarrow \infty$; (2) the phenomenon of transition of alignment to orientation is highly nonlinear, and as a result, the magnitude of the formed circular polarization of light is proportional to the third power of the intensity of the exciting light; (3) the effect is manifested only in the presence of an external magnetic field B. If BLE, only longitudinal orientation φ_0^1 arises; if the angle between B and E differs from 0 and $\pi/2$, transverse components of orientation $\varphi_{\pm 1}^1$ also arise.

The present article continues the analysis, started in Ref. 8, of the transition of alignment to orientation under the influence of DSE during excitation of lines of a broad spectral profile. Whereas Ref. 8 gave a simplified analysis that made it possible in model problems to obtain analytic expressions for the magnitude of the formed orientation of the ground state of the molecules and the relationship of this orientation to the degree of circularity of LIF, we shall now carry out numerical calculations, satisfying the accuracy requirements of the experiment, of the effect itself and expected signals for specific molecules for the purpose of indicating the magnitude of the effect in absolute terms.

The analysis is based on a system of equations that describes the process of optical pumping of molecules. The model is based on the following assumptions. The excitation is carried out with laser light of a broad spectral composition. The absorption rate is Γ_p . When the center of the exciting line does not coincide with the center of the absorption contour, a shift of the transition frequency ω_s takes place under action of quadratic DSE. In the excited state, the relaxation of the molecules is determined by radiative transitions and isotropic collisions with the buffer gas. The PM f_Q^K of the excited state relax at rates Γ_K .

The process of optical pumping is open, i.e., excited molecules have only a low probability $\Gamma_{J,J'}$ of return to the initial level as a result of a radiative transition. In the ground state, the relaxation is determined by the exchange of particles (transit of molecules through the laser beam) and energy (collisions) by the light-absorbing molecules with a thermostat. The thermostat is placed in the lower level only by the population. The PM φ_q^z of the ground state relax at rates γ_x . As a result, we obtain the following system of equations:⁸

$$f_Q^K = \Gamma_p \sum_{XK} {}^K F^{X\alpha} (\Phi^{(X)} \otimes \varphi^{(X)})_Q^K - \Gamma_p \left(\frac{2J'+1}{2J''+1} \right) \sum_{XK'} {}^K A_{1+}^{XK'} (\Phi^{(X)} \otimes f^{(K')})_Q^K + 2i\omega_s \left(\frac{2J'+1}{2J''+1} \right) \sum_{XK'} {}^K A_{1-}^{XK'} (\Phi^{(X)} \otimes f^{(K')})_Q^K - (\Gamma_K - iQ\omega) f_Q^K \quad (1a)$$

$$\varphi_q^z = -\Gamma_p \sum_{XK} {}^K A_{+}^{XK'} (\Phi^{(X)} \otimes \varphi^{(X')})_q^z + \Gamma_p \left(\frac{2J'+1}{2J''+1} \right) \sum_{XK} {}^K F^{XK} (\Phi^{(X)} \otimes f^{(K)})_q^z + 2i\omega_s \sum_{XK'} {}^K A_{-}^{XK'} (\Phi^{(X)} \otimes \varphi^{(X')})_q^z - (\gamma_x - iQ\omega) \varphi_q^z + \Gamma_{J,J'} C_x \delta_{Kx} \delta_{Qq} f_Q^K + \lambda_q^z \delta_{x0} \delta_{q0} \quad (1b)$$

Here the tensor Φ_ξ^X describes the polarization of the exciting light;¹ Ω and ω are the Zeeman splitting of the excited and ground levels; the rate constant λ_q^x characterizes the rate of occupation of the optically pumped-out ground state J'' in nonradiative processes; the coefficients ${}^K A_{1+}^{XK'}$, ${}^K A_{1-}^{XK'}$, ${}^K A_{+}^{XK'}$, ${}^K A_{-}^{XK'}$, ${}^K F^{X\alpha}$, ${}^K F_1^{XK}$ and C_x depend on the quantum numbers J'' and J' and are expressed in terms of the 6j and 9j symbols by means of the equations given in Ref. 8. [For more detail concerning the physical meaning of the individual terms in the system (1a), (1b), see Ref. 8.]

Substituting the PM f_Q^K of the excited state, which were obtained by solving the system of equations of motion, into the equation for the intensity of LIF¹

$$I \sim (-1)^{J''-J'} \sum_K (2K+1) \left\{ \begin{matrix} 1 & 1 & K \\ J' & J' & J_1'' \end{matrix} \right\} \sum_Q (-1)^Q f_Q^K \Phi_{-Q}^K \quad (2)$$

one can calculate the expected signals. In Eq. (2), the quantity in braces is the 6j symbol, and the tensor Φ_ξ^X describes the polarization of light distinguished in the recording.

This paper presents the results of a numerical solution of the system of Eq. (1a) and (1b) and calculation of the expected signals (2) for laser excitation of dimers. The computer program, written for steady-state excitation, makes it possible to solve the system of equations for practically any values of its parameters.

The analysis of the expected signals will be made from two points of view. First, we shall analyze the effect itself of the alignment-orientation transition and the magnitude of the expected degree of circularity of the fluorescence polarization. Second, we shall examine the influence of the effect of the alignment-orientation transition on the degree of linear polarization of LIF. Neglect of such influence may affect the accuracy of determination of such molecular characteristics as the relaxation rate, magnetic moment, and collisional relaxation cross section, which are measured in polarization experiments.⁹

In setting up the computer program for solving the system (1a), (1b), we used previously studied symmetry properties of the equations,^{10,11} modifying them because new terms proportional to $i\omega_s$ appeared in the equations.

We shall perform the calculation for a model situation that makes it possible in undisguised form to follow the manifestation of the alignment-orientation transition for the J''

rotational level of the ground state of the dimers. For this purpose, to preclude the influence of the excited state, we set $\Gamma_K \gg \Gamma_p$, which signifies the absence of induced transitions. We shall also assume $\Omega/\Gamma_K \ll 1$ for the relevant magnitudes of magnetic field B . Reverse spontaneous transitions to the initial level $\Gamma_{J,J'} = 0$ will be assumed absent. These assumptions hold quite well for a number of the dimers of interest.⁹ The geometry of the calculation is shown in the right-hand corner of Fig. 1. Observation along the magnetic field B is assumed. As was shown in Ref. 8, it is in this direction that the highest degree of circularity of LIF is expected. The quantity $C = (I_R - I_L)/(I_R + I_L)$ is recorded, where I_R and I_L are the clockwise- and counterclockwise-polarized components of the fluorescence. Fig. 1 shows the results for the type of dipole transition $Q \uparrow Q \downarrow (J'' = J' = J''')$ in the absorption-emission cycle. It was assumed in the calculation that $\gamma_x = \gamma = 1.0 \mu\text{sec}^{-1}$, $\Gamma_K = \Gamma = 10^4 \mu\text{sec}^{-1}$, $\Omega = \Gamma_{J,J'} = 0$, $J'' = J' = J'' = 2$. Let us first follow the dependence of the magnitude of the expected signal, i.e., the degree of circularity of LIF, on Γ_p at constant ω_s . For this purpose, we compare curves 2, 4, and 5. It is evident that at low absorption rates, the signal has a shape similar to a dispersion shape, with an extremum at the point $\omega/\gamma = 0.5$, as was predicted in Ref. 8. Figure 1 shows a portion of the $C(\omega/\gamma)$ curve for positive values of the argument. The curves for negative ω/γ are symmetric to those shown relative to the origin of the coordinates. As Γ_p increases, the signal amplitude increases rapidly at first, but then this increase slows down (curve 2), and at the same time, the signal broadens.

If Γ_p is kept constant and the signal is studied as a function of the magnitude of the Stark shift (curves 1, 3, and 5), it becomes evident that as ω_s increases, the signal amplitude grows rapidly. The degree of circularity in this case reaches values $> 1\%$. Only a slight broadening of the signals takes

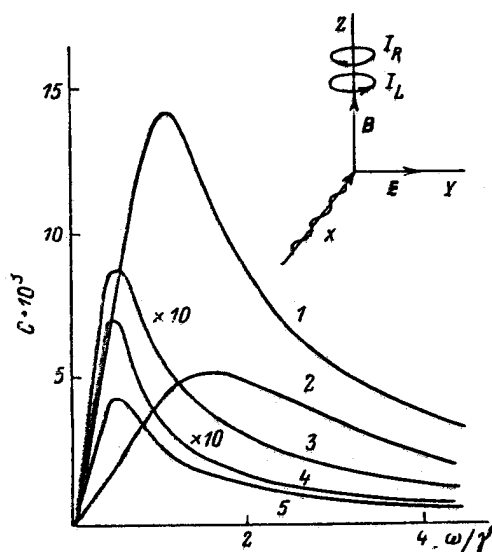


FIG. 1. Degree of circular polarization of LIF vs the parameter ω/γ . 1— $\Gamma_p = 1.0 \mu\text{sec}^{-1}$, $\omega_s = 5.0 \mu\text{sec}^{-1}$; 2— $\Gamma_p = 10.0$, $\omega_s = 1.0 \mu\text{sec}^{-1}$; 3— $\Gamma_p = 1.0$, $\omega_s = 0.2 \mu\text{sec}^{-1}$; 4— $\Gamma_p = 0.1$, $\omega_s = 1.0 \mu\text{sec}^{-1}$; 5— $\Gamma_p = 1.0$, $\omega_s = 1.0 \mu\text{sec}^{-1}$.

place. Such signals can be observed alone, and can have an appreciable interfering influence on the signals of the dependence of the circular polarization of LIF on ω , signals used for determining a number of molecular characteristics.¹² The situation is also complicated by the fact that in many experiments, the value of ω_s is practically unknown.

For other types of molecular transitions leading to a change by ± 1 in the value of the angular-momentum quantum number, the expected signals have a similar shape.

In the model being analyzed, the influence of the dynamic Stark effect on a molecule in an external magnetic field gives rise to orientation of the angular momenta of molecules in the ground state. For the experimental geometry under consideration, when the directions of excitation, linear polarization of light and external magnetic field are mutually orthogonal, the main type of orientation formed is longitudinal orientation φ_0^1/φ_0^0 , i.e., the orientation of the angular momenta of the molecule along or against the external magnetic field. Figure 2 shows the magnitude of this orientation for the type of transitions $Q \uparrow Q \downarrow$. All the parameters in the calculation are the same as those in the calculation of the curves of Fig. 1, with the exception of those given in the caption to Fig. 2. It is evident that in the dynamic Stark effect, in the presence of an external magnetic field, a significant orientation of the angular momenta of the ground state of the molecules can be achieved. In some cases, this orientation can even exceed the magnitude of the longitudinal alignment. Figure 3 shows signals related to the alignment-orientation transition for transitions excited by standard gas lasers in real molecules, where in addition to the phenomenon studied, both spontaneous and induced reverse transitions are present. These signals are also affected by the magnetism of the excited level. In Fig. 3(a), the transition $J'' = 18 \rightarrow J' = 17 \rightarrow J'' = 16$ is examined in the case of the Na_2 molecule in the geometry of Fig. 1.¹³ In the calculation, it was assumed that $\gamma_x = \gamma = 0.3 \mu\text{sec}^{-1}$, $\Gamma_K = \Gamma = 83.3 \mu\text{sec}^{-1}$, $\Gamma_{J,J'} = 0.83 \mu\text{sec}^{-1}$, $\omega/\Omega = -1$. It is evident that even at relatively high values of angular momentum, the amplitude of the expected signal may exceed 1%.

Figure 3(b) shows the influence of the orientation-alignment transition during recording, along a magnetic field, of the degree of linear polarization of LIF. As before, the polarization of the exciting light is along the y axis. The calculation was carried out for the transition $J'' = 2 \rightarrow J' = 1 \rightarrow J'' = 0$ of the Li_2 molecule.¹⁴ It was as-

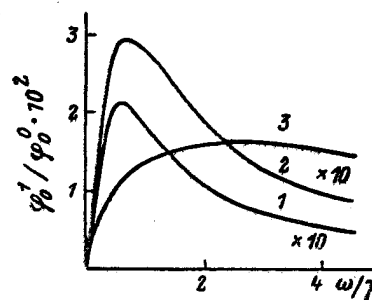


FIG. 2. Magnitude of longitudinal orientation φ_0^1/φ_0^0 vs the parameter ω/γ , $\omega_s = 1.0 \mu\text{sec}^{-1}$, Γ_p (μsec^{-1}): 1—0.1, 2—1.0, 3—10.0.

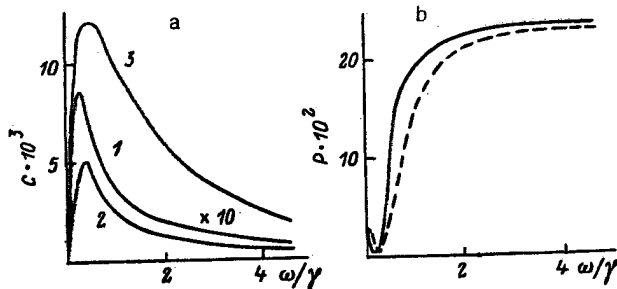


FIG. 3. Degree of circular C and linear P polarization of LIF vs the parameter ω/γ . (a) Na_2 molecule: $\Gamma_p = \omega_S (\mu\text{sec}^{-1})$: 1—0.3, 2—1.0, 3—3.0; (b) Li_2 molecule.

sumed that $\gamma_x = \gamma = 0.3 \mu\text{sec}^{-1}$, $\Gamma_K = \Gamma = 55.5 \mu\text{sec}^{-1}$, $\Gamma_{J,J'} = 0.55$, $\Gamma_p = 3.0 \mu\text{sec}^{-1}$, $\Omega/\omega = -0.34$. For the continuous curve, $\omega_S = 0$, and for the dashed curve, $\omega_S = 3.0 \mu\text{sec}^{-1}$. It is evident that the dashed curve is broadened relative to the continuous one. Since the shape of the LIF repolarization curve can serve to determine the characteristics of the rotational level of the ground state of the molecules,⁹ it follows that in order to ensure the accuracy of the results obtained, allowance for the influence of the dynamic Stark effect can play a definite role.

Finally, we should touch on the possibility of the case with a large ratio ω_S/Γ_p occurring in an experiment. Using the explicit form of the relationship of Γ_p and ω_S to the spectral contour of the excitation line $I(\nu)$,¹⁵ one can write the ratio ω_S/Γ_p in the approximation of excitation by a broad line,¹⁶ in the form

$$\omega_S/\Gamma_p = \frac{1}{2\pi} v \cdot \text{p.} \int \frac{I(\nu) d\nu}{(\nu - \nu_0) I(\nu_0)}, \quad (3)$$

where ν_0 is the frequency of the absorbing transition, and $v \cdot \text{p.}$ denotes the principal value of the integral (see Ref. 17 concerning the correspondence of the broad-line approximation of a real situation in dimers). Integrating Eq. (3) for a Lorentzian shape of the exciting line, we obtain $\omega_S/\Gamma_p = (\nu_0 - \nu_L)/\Delta\nu_L$, where ν_L is the frequency of the center of the exciting line contour, and $\Delta\nu_L$ is its semihalf width. In the case of a Gaussian excitation contour, the integral (3) should be found numerically. Figure 4 shows $\log(\omega_S/\Gamma_p)$ as a function $\delta/\Delta\nu_G$, where δ is the detuning of the absorption line from the center of the exciting line, and $\Delta\nu_G$ indicates the distance from the center of the exciting line at which the excitation line intensity decreased e -fold.

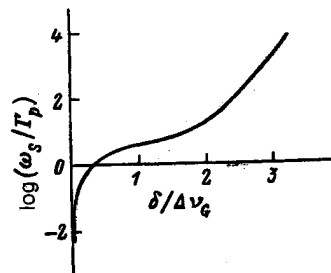


FIG. 4. $\log(\omega_S/\Gamma_p)$ vs $\delta/\Delta\nu_G$ for a Gaussian excitation contour.

From the given integration results one can conclude that a situation in which ω_S exceeds Γ_p severalfold is entirely possible.

The above analysis shows that inclusion of the dynamic Stark effect in the discussion of the interaction of intense laser radiation of a broad spectral profile with dimers placed in an external magnetic field may significantly affect the interpretation of the results obtained and the accuracy of the experimental determination of the characteristics of states.

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