Orientation of molecules in the ground state by linearly polarized light with a wide spectral profile

M. P. Auzinsh

An orientation-alignment transition is analyzed for the ground state of molecules subjected to the dynamic Stark effect. Analytic expressions are derived for the orientation value. It is shown that, first, orientation of angular momenta resulting from the action of the dynamic Stark effect is a nonlinear process which depends quadratically on the intensity of the irradiating light; second, it is a quantum effect and disappears for states with large angular momentum; and, third, it occurs only in the presence of an external magnetic field.

Alignment of the excited state of the ensemble of atoms or molecules occurs as a result of absorption of linearly polarized light. For molecules in the gas phase, in particular, this means that there appears a preferred plane in which the optically excited molecules predominantly rotate.

Various mechanisms of an orientation-alignment transition have been studied, i.e., the appearance of circularly polarized radiation in the fluorescence of initially aligned atoms or molecules.[1-3] To achieve such a transition an external anisotropic perturbing factor—a magnetic field or anisotropic collisions is necessary in addition to the exciting light.

When the frequency of the monochromatic exciting light is detuned slightly from the frequency of the resonance transition of the atomic particles in a magnetic field, the occurrence of orientation is easily explained even for weak exciting light, when the absorption rate Γ_p is much lower than both the excited-state relaxation Γ and the ground-state relaxation rate γ. In this case the magnetic field splits the excited state into a series of magnetic sublevels. The sublevels with magnetic quantum numbers M and $-M$ are filled somewhat differently as a result of the absorption—this is what indicates the appearance of orientation of this state.[4]

If the weak exciting light is in resonance or its spectral profile is somewhat wider than the absorption line, then the

effect described cannot occur. However, for intense exciting light with a wide spectral profile, in the case when the center of the profile of the exciting light does not coincide with the absorption line and in the presence of an external magnetic field, an orientation-alignment transition of the excited state can occur as a result of the dynamic Stark effect.[5] This requires that the Stark splitting of the absorption lines

$$\omega_S = \frac{1}{\hbar^2} \text{ v.p.} \int \frac{I(\omega_l) |\langle J' \| \hat{d} \| J'' \rangle|^2 \omega_0}{2(\omega_l^2 - \omega_0^2)} d\omega_l, \qquad (1)$$

where $\langle J' \| \hat{d} \| J'' \rangle$ is the reduced matrix element of the dipole transition from the ground state with angular momentum J'' into a state with angular momentum J', ω_0 is the frequency of this transition, and $I(\omega_l)$ is the spectral profile of the excitation line, be comparable to the natural width of the excited level $2\pi/\Gamma$. This width is assumed to be infinitely small only compared with the line width of the exciting light. An effect of this type has been studied by Kotlikov and Chaika[6,7] using both a classical model and a quantum-mechanical approach.

Along with the effects considered, optical pumping of the ground level of the transition[8,9] can also strongly influence the polarization of the resonance fluorescence of atoms and molecules.

It is shown in this paper that the dynamic Stark effect in a magnetic field can also bring about an orientation-alignment transition of even the ground state of atomic particles aligned as a result of optical pumping. This occurs at significantly lower intensities of the exciting light, since in this case the Stark splitting ω_s must be compared with the width of the ground level of the resonance transition $2\pi/\gamma$. Such an effect can substantially influence the laser-induced fluorescence of atoms and molecules.

To describe the interaction of an ensemble of gas-phase molecules with light having a wide spectral profile of arbitrary intensity we shall use the equations of motion of the polarization moments (PM). They are obtained from the equations of motion for the density operator[10] written in matrix form.[11] Expanding the latter equations in irreducible tensor operators and taking into account the dynamic Stark effect we obtain

$$f_Q^K = \Gamma_p \sum_{Xx} {}^X F^{Xx} \{\Phi^{(X)} \otimes \varphi^{(x)}\}_Q^K$$

$$- \Gamma_p \left(\frac{\Pi_{J'}}{\Pi_{J''}}\right)^2 \sum_{XK'} {}^X A_{1+}^{XK'} \{\Phi^{(X)} \otimes f^{(K')}\}_Q^K.$$

$$+ 2i\omega_S \left(\frac{\Pi_{J'}}{\Pi_{J''}}\right)^2 \sum_{XK'} {}^X A_{1-}^{XK'} \{\Phi^{(X)} \otimes f^{(K')}\}_Q^K - (\Gamma_K - iQ\Omega) f_Q^K,$$

$$(2a)$$

$$\varphi_q^x = -\Gamma_p \sum_{Xx'} {}^x A_+^{Xx'} \{\Phi^{(X)} \otimes \varphi^{(x')}\}_q^x$$

$$+ \Gamma_p \left(\frac{\Pi_{J'}}{\Pi_{J''}}\right)^3 \sum_{XK} {}^x F_1^{XK} \{\Phi^{(X)} \otimes f^{(K)}\}_q^x$$

$$+ 2i\omega_S \sum_{Xx'}^x A_-^{Xx'} \{\Phi^{(X)} \otimes \varphi^{(x')}\}_q^x - (\gamma_x - iq\omega) \varphi_q^x$$

$$+ \Gamma_{J',J''} C_x \delta_{Kx} \delta_{Qq} f_Q^K + \lambda_q^x \delta_{x0} \delta_{q0}. \qquad (2b)$$

Here f_Q^K and φ_q^x are the polarization moments of the excited and ground states and Γ_K and γ_x are their relaxation rates,

$${}^X F^{Xx} = \frac{\Pi_3, \Pi_x^2}{\Pi_{J''K}} (-1)^{X+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ x & J'' & J'' \end{Bmatrix}, \qquad (3)$$

$${}^X A_{\pm}^{Xx'} = \frac{1 \pm (-1)^{1+X+x'}}{2} \frac{\Pi_{J'}^2, \Pi_{Xx'}}{\Pi_x} (-1)^{J'-J''+x'} \begin{Bmatrix} x & X & x' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J' \end{Bmatrix}, \qquad (4)$$

$$C_x = (-1)^{J'-J''+x+1} \Pi_{J''J'} \begin{Bmatrix} J'' & J'' & x \\ J' & J' & 1 \end{Bmatrix}. \qquad (5)$$

Expressions for the coefficients ${}^X A_{1\pm}^{Xx'}$ and ${}^X F_1^{XK}$ are obtained from Eqs. (4) and (3) by exchanging J'' and J'. In Eqs. (3)-(5) the braces denote 9j- and 6j-symbols.[12] The functions Φ_ξ^X describe the polarization of the exciting light,[13,14] and the factor $\Pi_{ab\dots} = \sqrt{(2a+1)(2b+1)\dots}$. The symbol $\otimes$ denotes the irreducible tensor product. In Eqs. (2a) and (2b) the first term describes light absorption, the second term describes stimulated emission, the third term describes the effect of the dynamic Stark effect, and the fourth term describes the relaxation of the polarization moment and the action of an external magnetic field leading to Zeeman splitting ω and Ω of the ground and excited states. The last two terms in Eq. (2b) describe reverse spontaneous transitions and isotropic filling of the lower level.

If an ensemble of atomic particles is excited by linearly polarized light when only the Φ_ξ^X components with rank $X = 0,2$ differ from zero,[13] then the angular momenta become aligned only for $\omega_s = 0$ in the ensemble[1] (these components describe the polarization moments of even rank K and x), since the coefficients ${}^K F^{Xx}$, ${}^x F_1^{XK}$, ${}^K A_{1+}^{XK'}$, and ${}^x A_+^{Xx'}$ equal zero if the sum of the upper indexes is odd.

In the case ω_s differs from zero an orientation-alignment transition occurs, since the ${}^K A_{1-}^{XK'}$ and ${}^x A_-^{Xx'}$ coefficients are different from zero only if the sum of the upper indexes is odd. In this case the fluorescence is expected to be circularly polarized.

The ${}^x A_-^{Xx'}$ coefficient characterizes the efficiency of the orientation-alignment transition for the ground state and the ${}^K A_{1-}^{XK'}$ coefficient characterizes the same for the excited state. Using explicit expressions for the 6j symbols,[12] for example for the ground state, we find for the three allowed types of molecular transitions $Q(J'' = J')$, $P(J'' = J' + 1)$, and $R(J'' = J' - 1)$

$${}^1 A_-^{22}(Q) = \frac{5[3 - 4J''(J''+1)]}{J''(J''+1)\sqrt{3(2J''-1)(2J''+3)}},$$

$${}^1 A_-^{22}(P) = \frac{5}{\sqrt{3}} \sqrt{\frac{2J''-1}{2J''+3}} \frac{2J''^2 + 5J''+3}{J''(J''-1)(2J''+1)},$$

$${}^1 A_-^{22}(R) = \frac{5}{\sqrt{3}} \frac{\sqrt{(2J''+3)(2J''-1)}}{(2J''+1)(J''+1)}.$$

These quantities show the efficiency of a quadrupole-alignment transition ($x' = 2$) under the action of linearly polarized light ($X = 0,2$) to dipole orientation ($x = 1$). As J'' increases the coefficients $|{}^1 A_-^{22}|$ decrease (cf. Fig. 1), approaching

$${}^1 A_-^{22}(P) = {}^1 A_-^{22}(R) = \frac{5}{\sqrt{3}} \frac{1}{J''};$$

$${}^1 A_-^{22}(Q) = -\frac{10}{\sqrt{3}} \frac{1}{J''}$$

asymptotically for large J''.

We solve the system of Eqs. (2a) and (2b) for the case of no stimulated or reverse spontaneous transitions $\Gamma_p \ll \Gamma_K$,
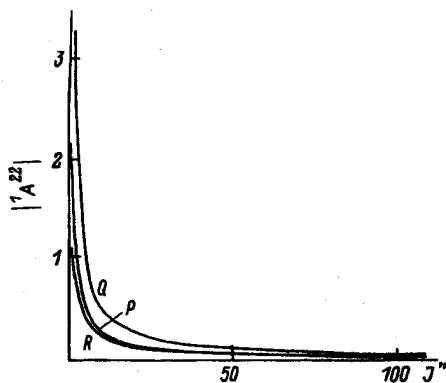
FIG. 1. Dependence of the absolute value of the coefficient $^1A^{22}$ on the angular momentum J'' of the lower level of the transition.

$\Gamma_{J'J'} = 0$, which is well satisfied for a series of diatomic molecules excited by gas lasers.[15] For Q-type transitions with $J'' = J' = 1$, expanding the solution in a power series in the parameters ω_S/γ_x and Γ_p/γ_x, we find φ^1_q. If the polarization vector of the exciting light is described by spherical angles θ and φ, then

$$\Phi^0_0 = -1/\sqrt{3}, \quad \Phi^1_{\pm} = 0, \quad \Phi^2_0 = (3\cos^2\theta - 1)/\sqrt{30},$$

$$\Phi^2_{\pm 2} = \sin^2\theta e^{\pm 2i\varphi}/2\sqrt{5},$$

$$\Phi^2_{\pm 1} = \pm\sin\theta\cos\theta e^{\pm i\varphi}/\sqrt{3},$$

and in second order of the expansion we find

$$\varphi^1_0 = \frac{\omega_S\Gamma_p\omega\sqrt{2}}{12\gamma_1}\sin^2\theta\left(\frac{\sin^2\theta}{\gamma_1^2 + 4\omega^2} + \frac{\cos^2\theta}{\gamma_1^2 + \omega^2}\right),$$

$$\varphi^1_1 = -(\varphi^1_{-1})^* = t e^{i\varphi}\frac{\omega_S\Gamma_p}{24(\gamma_1 - i\omega)}\left[\sin^2\theta\cos\theta\left(\frac{\gamma_2 + 2i\omega}{\gamma_1^2 + 4\omega^2} - \frac{\gamma_2 - i\omega}{\gamma_1^2 + \omega^2}\right)\right.$$
$$\left. + (3\cos^2\theta - 1)\cos\theta\sin\theta\left(\frac{\gamma_2 + i\omega}{\gamma_1^2 + \omega^2} - \frac{1}{\gamma_2}\right)\right].$$

It is obvious that when magnetic field **H** (which defines the z axis) and the **E** vector of the exciting light are orthogonal ($\theta = \pi/2$), only longitudinal orientation φ^1_0 occurs. In other cases transverse orientation $\varphi^1_{\pm 1}$ also is produced.

It is of interest to consider the case of absorption with $J'' = J' = 2$. Since the maximum possible PM rank equals $2J$, orientation of rank x greater than 1 is possible in this case. By analogy to the last example we obtain for the case of orthogonal **E** and **H**

$$\varphi^1_0 = \frac{\omega_S\Gamma_p\omega}{\gamma_1(\gamma_1^2 + 4\omega^2)}\frac{7\sqrt{2}}{60\sqrt{3}},$$

$$\varphi^3_0 = -\frac{\omega_S\Gamma_p\omega}{\gamma_3(\gamma_1^2 + 4\omega^2)}\frac{\sqrt{14}}{105},$$

$$\varphi^3_2 = (\varphi^3_{-2})^* = i\frac{\omega_S\Gamma_p(\gamma_2 + 2i\omega)}{\gamma_3^2 + 4\omega^2}\frac{\sqrt{7}}{42\sqrt{15}}\left(\frac{\gamma_2 + 2i\omega}{\gamma_1^2 + 4\omega^2} - \frac{1}{\gamma_2}\right).$$

It is of interest to note that the dependence on the Zeeman splitting ω is identical for φ^1_0 and φ^3_0. Besides the longitudinal components φ^x_0, transverse components $\varphi^3_{\pm 2}$ occur also. For states with angular momentum $J'' > 2$ the longitudinal orientation χ^x_0 with rank $x \geqslant 5$ in the first nonzero approximation will have the same dependence on ω as do φ^1_0 and φ^3_0.

The foregoing analysis shows that, first, orientation of angular momenta resulting from the dynamic Stark effect is a nonlinear process which depends quadratically upon the external radiation field, $\sim\omega_S\Gamma_p$; second, the occurrence of orientation is a quantum effect, which disappears in the limit $J \to \infty$; third, orientation appears only in the presence of an external magnetic field, and in the geometry **E⊥H** only the longitudinal projection φ^1_0 arises for dipole orientation φ^1_q, while components with even values of index q occur for orientations of higher rank $x \geqslant 3$.

When the condition $\Gamma_p \ll \Gamma_K$ is not satisfied, i.e., in the presence of stimulated transitions, an orientation-alignment transition similar to that in the ground state also occurs in the excited states of the molecules.

We consider below how orientation of the ground state of molecules leads to the appearance of circular polarization in laser-induced fluorescence (LIF). The same light wave that creates the orientation transfers it to the excited state. For example, for the **E⊥H** geometry and in the absence of stimulated transitions, according to Eq. 2(a),

$$f_0^1 = \frac{\Gamma_p}{\Gamma_1}\left[\left(-\frac{^1F^{01}}{\sqrt{3}} + \frac{^1F^{21}}{5\sqrt{3}}\right)\varphi^1_0 + \frac{^1F^{23}}{\sqrt{35}}\operatorname{Re}\varphi^3_2\right].$$

For observation in the direction of the magnetic field and recording the difference of the intensity of right- and left-circularly polarized LIF, using the formulas for intensity[13]

$$I \sim (-1)^{J''-J_1''}\sum_K \Pi_K\begin{Bmatrix}1 & 1 & K \\ J' & J' & J_1''\end{Bmatrix}\sum_Q (-1)^Q f^K_Q \Phi^K_{-Q},$$

where J_1'' is the angular momentum of the final state in emission and the tensor Φ^K_Q describes the polarization of the recorded LIF, we obtain

$$I_R - I_L \sim (-1)^{J''-J_1''}\sqrt{6}\begin{Bmatrix}1 & 1 & 1 \\ J' & J' & J_1''\end{Bmatrix}f_0^1.$$

Thus it is obvious that the difference signal is entirely determined by orientation occurring as a result of the dynamic Stark effect.

To investigate the expected signals in more detail without restrictions on the relaxation rates of the ground and excited states and the absorption rate it is necessary to solve the system of Eqs. (2a) and (2b) numerically on a computer.

[1] M. Lombardi, C. R. Acad. Sci. Ser. B 265, 191 (1967).

[2] V. N. Rebane, Opt. Spektrosk. 24, 309 (1968) [Opt. Spectrosc. (USSR) 24, 163 (1968)].

[3] E. N. Kotlikov, Author's Abstract of Doctoral Dissertation (Leningrad, 1982), p. 415.

[4] A. C. Mitchell and M. W. Zemansky, Radiation and Excited Atoms (Cambridge Univ. P., 1971; ONTI, Moscow, 1937).

[5] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (Dover, 1975; Moscow, 1959).

[6] E. N. Kotlikov and M. P. Chaika, Opt. Spektrosk. 55, 242 (1983) [Opt. Spectrosc. (USSR) 55, 142 (1983)].

[7] E. N. Kotlikov and M. P. Chaika, in Abstracts of the Seventh All-Union Conference on TAAS (Tbilisi, 1981).

[8] A. Kastler, J. Phys. Radium 11, 225 (1950).

[9] R. E. Drullinger and R. N. Zare, J. Chem. Phys. 59, 4225 (1973).

[10] C. Cohen-Tannoudji, Ann. Phys. 7, 423 (1962).

[11] E. N. Kotlikov and V. A. Kondrateva, Opt. Spektrosk. 48, 667 (1980) [Opt. Spectrosc. (USSR) 48, 367 (1980)].

[12] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (Leningrad, 1975), p. 439.

[13] M. I. Dyakonov, Zh. Eksp. Teor. Fiz. 47, 2213 (1964) [Sov. Phys. JETP 20, 1484 (1964)].

[14] M. P. Auzinsh and R. S. Ferber, Opt. Spektrosk. 66, 275 (1989) [Opt. Spectrosc. (USSR) 66, 158 (1989)].

[15] R. S. Ferber, Energy Transfer Processes in Metal Vapors (Riga, 1983), p. 3.