Optical pumping of diatomic molecules in the electronic ground state: Classical and quantum approaches

M. P. Auzin'sh and R. S. Ferber
Department of Physics and Mathematics, Latvian University, Riga, Latvia 226098, U.S.S.R.
(Received 2 April 1990)

Optical pumping of the electronic ground state of molecules has been investigated under conditions of plane, elliptically, and circularly polarized light broadband excitation. The analysis has been performed assuming arbitrary angular momentum values, and applying the apparatus of polarization moments, the latter forming the coefficients in the expansion of the density matrix over irreducible tensor operators, including simplifications due to asymptotic limits for large momentum values. In addition to accounting for the external magnetic field, attention has been also given to the dynamical Stark effect arising from the absence of coincidence between the centers of the exciting line and the absorption line. An alternative classical description is also proposed using multiple moments as coefficients of the expansion of a classical quasidensity of states over spherical harmonics. The equivalence of both approaches of description in the limit of infinitely large angular moments is demonstrated, and the meaning of the origin of coherence is clarified, as well as its destruction by the magnetic field in the classical description of the system.

I. INTRODUCTION

In 1950 Kastler predicted[1] and later effected[2] a method of creating a nonequilibrated population of magnetic sublevels, as well as sublevels of hyperfine structure (HFS) of an atomic ground state. This method made studies of magnetic moments possible, as well as studies of hyperfine interaction, disorientation cross sections, energy-level shifts, and other atomic characteristics. For a review, see, e.g., Refs. 3–5, and references therein.

In the case of molecules, even after the appearance of lasers, as a result of certain prejudices discussed in Ref. 6, optical pumping (alignment) of the rovibronic ground state (RVS) was only begun in 1969.[6,7] Further work led to registering and studying interference phenomena in systems of degenerate ground-state sublevels (Hanle effect[8]), of nondegenerate sublevels (beat resonance),[9] and of quantum beats in the kinetics of transient processes.[10] Application of these methods to molecules in sodium, potassium,and tellurium vapors made it possible to determine summary effective relaxation cross sections and magnetic g factors of corresponding dimers in the fixed RVS. Optical pumping was applied to sodium-dimer-containing beams[11] in order to register resonance signals between HFS levels of $Na_2(X\,^1\Sigma_g^+)$ and to determine the HFS constants.

A description of the signals of optical pumping and the interference of magnetic levels of RVS is by no means a trivial problem for molecules with a high value of angular momentum ($J \gg 1$, as a rule). This applies also to essential peculiarities of the balance between radiational and collisional processes. The main stress in the present work has been placed on an analysis of the origin of alignment and orientation of angular moments in the electronic ground state under the effect of light absorption, as well as on a study of this effect in laser-induced fluorescence (LIF). It is necessary to point out that there exists a large number of works (cf., e.g., Refs. 12–16, and sources quoted therein) in which methods are worked out for the determination of parameters characterizing alignment and orientation in the electronic ground state for diatomic molecules by means of polarization studies in LIF. However, in these works it is not the mechanism of the appearance of anisotropy in angular moments that is discussed, but rather methods of testing of already existing alignment or orientation.

In the framework of the present studies we pay attention to the interaction between laser radiation of wide spectral composition and molecules in the presence of an external magnetic field. The intensity of laser radiation is considered such that the rate of optical pumping should be comparable to that of ground-state relaxation. In order to analyze such processes Cohen-Tannoudji[15] in 1962 obtained equations of motion for the operator of state density (statistic operator). A further development of this approach[16,17] made it possible to obtain and analyze equations of motion for the expansion coefficients of the density matrix over irreducible tensor operators. These coefficients are usually called polarization moments (PM's), and they are directly connected with alignment and orientation of the ensemble of particles. Equations of motion of PM's are conveniently expressed in a compact form, as proposed by Okunevich.[9]

The primary aim of the present work is to obtain maximally complete equations of PM motion for states with arbitrary angular momentum values (Sec. III). In addition to spontaneous and stimulated processes, collisional relaxation, and relaxation in external magnetic fields, we must also consider the influence of the dynamical Stark effect[18] under broadband excitation. This effect arises from noncoincidence between the centers of the excitation contour and the resonance transition frequency. Explicit expressions are given for the calculation of PM's in

the case of elliptical polarization of the exciting light.

However, in states with high-angular-momentum values, as is the case in most experiments with dimers under discussion, there are possibilities of simplifying the problem. Indeed, the conservation of angular momentum is most simply accounted for in the interaction between light and the molecule, if we employ asymptotic expressions[19] for $J\to\infty$ in the coefficients of moment addition. At the same time there exists a consistently classical method of description for such states. It is based on the evolution of the classical density-of-states probability.[20,21] However, such an approach does not make full use of the simplifications following from symmetry properties of the system. As already pointed out by the authors of the above-cited papers,[20,21] this disadvantage can be overcome by expanding the classical density of probability over spherical functions. In the present work (Sec. V) equations of motion have been obtained for the coefficients of such an expansion. The above approach has been compared with equations of PM motion through which we can discuss the concept and physical meaning of coherence in the classical limit $J\to\infty$. In the analysis of the equations obtained, the mathematical operations have been performed comprehensively for a large number of cases occurring in experimental practice. This makes it possible to apply the results thus obtained directly to the analysis of experimental data.[8-10] As examples, degrees of polarization or of anisotropy of radiation have been obtained for different excitation conditions at arbitrary J values, accounting for effects of optical alignment and orientation of the ground state.

II. GENERAL EQUATIONS OF DENSITY-MATRIX MOTION

When a set of molecules is illuminated by a laser beam that causes a rovibronic transition, cf. Fig. 1, an anisotropy is created in the spatial distribution of the angular momenta J'' and J' in ground and excited molecular states. If in this process some prevailing plane of molecular rotation is created, then the set is aligned. If the set possesses helicity, it is said to be oriented. The degree of orientation and alignment of molecules in both excited and ground states can be determined by means of an analysis of the intensity and polarization of LIF $J'\to J_1''$.

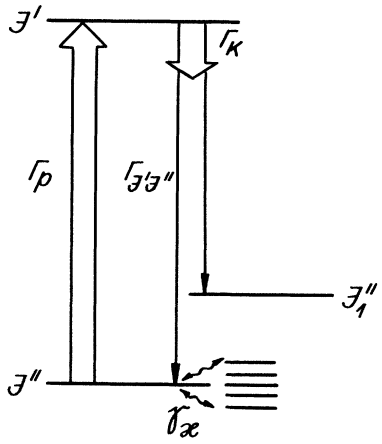

FIG. 1. Scheme of optical pumping in the case of diatomic molecule optical transitions between separate rovibronic levels $(\beta'',v'',J'')\to(\beta',v',J')\to(\beta'',v_1'',J_1'')$ where v denote vibrational numbers of the ground state β'' and the excited state β'.

For analyzing the interaction between light and the molecular gas according to the scheme shown on Fig. 1, we shall use as a basis the equations of motion of the density matrix in the $|JM\rangle$ representation.[15] In this representation the existence of molecular alignment means that the probability of finding the molecule in a state M (or $-M$) differs from that of finding it in a state with different M' (or $-M'$). In the case of molecular orientation the probabilities of finding the molecule in states M and $-M$ differ. The equations of motion of the density matrix $f_{MM'}$ for the excited state and $\varphi_{\mu\mu'}$ for the ground state have the following form, in the approximation of the broadband excitation line:[17]

$$\dot f_{MM'}=\Gamma_p\sum_{\mu,\mu'}\langle M|\mathbf{e}_a\cdot\mathbf{r}|\mu\rangle\varphi_{\mu\mu'}\langle\mu'|\mathbf{e}_a^*\cdot\mathbf{r}|M'\rangle-\left[\frac{\Gamma_p}{2}-i\omega_S\right]\times\sum_{M'',\mu}\langle M|\mathbf{e}_a\cdot\mathbf{r}|\mu\rangle\langle\mu|\mathbf{e}_a^*\cdot\mathbf{r}|M''\rangle f_{M''M'}-\left[\frac{\Gamma_p}{2}+i\omega_S\right]\times\sum_{M'',\mu}f_{MM''}\langle M''|\mathbf{e}_a\cdot\mathbf{r}|\mu\rangle\langle\mu|\mathbf{e}_a^*\cdot\mathbf{r}|M'\rangle-\sum_{M_1,M_1'}\Gamma_{MM'}^{M_1M_1'}f_{M_1M_1'}-i(M-M')\omega_{J'}f_{MM'}\,, \tag{1a}$$

$$\dot\varphi_{\mu\mu'}=-\left[\frac{\Gamma_p}{2}-i\omega_S\right]\sum_{\mu'',M}\varphi_{\mu\mu''}\langle\mu''|\mathbf{e}_a^*\cdot\mathbf{r}|M\rangle\langle M|\mathbf{e}_a\cdot\mathbf{r}|\mu'\rangle-\left[\frac{\Gamma_p}{2}+i\omega_S\right]\sum_{\mu'',M}\langle\mu|\mathbf{e}_a^*\cdot\mathbf{r}|M\rangle\langle M|\mathbf{e}_a\cdot\mathbf{r}|\mu''\rangle\varphi_{\mu''\mu'}+\Gamma_p\sum_{M,M'}\langle\mu|\mathbf{e}_a^*\cdot\mathbf{r}|M\rangle f_{MM'}\langle M'|\mathbf{e}_a\cdot\mathbf{r}|\mu'\rangle-\sum_{\mu_1,\mu_1'}\gamma_{\mu\mu'}^{\mu_1\mu_1'}\varphi_{\mu_1\mu_1'}-i(\mu-\mu')\omega_{J''}\varphi_{\mu\mu'}+\sum_{M,M'}\Gamma_{\mu\mu'}^{MM'}f_{MM'}+\lambda\delta_{\mu\mu'}\,. \tag{1b}$$

Frequencies $\omega_{J'}$ and $\omega_{J''}$ are equal to the Zeeman splitting of magnetic sublevels in excited and ground states in an external magnetic field **B**. The quantization axis **z** is chosen along **B**. The constants $\Gamma^{M_1M_1'}_{MM'}$ and $\gamma^{\mu_1\mu_1'}_{\mu\mu'}$ determine the relaxation rates of the excited and ground states, but $\Gamma^{MM'}_{\mu\mu'}$ determines that of spontaneous back transitions.

The factor

$$\Gamma_p=\frac{2\pi}{\hbar^2}|\langle J'\|r\|J''\rangle|^2e^2i(\omega_0) \tag{2}$$

determines the absorption rate, while

$$\omega_S=\frac{1}{\hbar^2}\int\frac{|\langle J'\|r\|J''\rangle|^2e^2i(\omega_l)}{\omega_l-\omega_0}d\omega_l \tag{3}$$

is the frequency shift as a result of dynamic Stark effect.[18,22] Here $\langle J'\|r\|J''\rangle$ is the reduced matrix element for the $J''\rightarrow J'$ transition, cf. Fig. 1, e is the electron charge, ω_0 is the resonance transition frequency, and ω_l is the laser frequency with spectral intensity density $i(\omega_l)$. The unit vector $\mathbf{e}_a$, entering into the dipole transition matrix element $\langle M|\mathbf{e}_a\cdot\mathbf{r}|\mu\rangle$, describes the polarization of the exciting light. The term $\lambda\delta_{\mu\mu'}$ characterizes the isotropic relaxation of the ground state in interaction with the thermostat formed by molecules not affected by optical action. The viability of such an approximation in certain circumstances is justified by the results of Ref. 23. System (1) is formulated under the assumption of excitation by means of a line of wide spectral range, i.e., when the equations do not contain any dependence on the velocity of particle motion.

The LIF intensity in the $J'\rightarrow J_1''$ transition, cf. Fig. 1, with polarization $\mathbf{e}_f$ is determined by the excited-level matrix $f_{MM'}$[24]

$$I=I_0\sum_{M,M',\mu}f_{MM'}e^2\langle M'|\mathbf{e}_f\cdot\mathbf{r}|\mu\rangle\langle\mu|\mathbf{e}_f^*\cdot\mathbf{r}|M\rangle\ , \tag{4}$$

where I_0 is a proportionality coefficient.

Let us consider the following example. Let the set of molecules be excited by a light wave that is polarized along A_η, $\eta=0,\pm1$, in a cyclic system of coordinates[19]

$$A_0=A_z,\quad A_{\pm1}=\mp(A_x\pm iA_y)/\sqrt{2}\ . \tag{5}$$

This means excitation by light either plane polarized along the **z** axis, or circularly polarized and propagating along the **z** axis, cf. Fig. 2.

Let us assume that $\Gamma_p\ll\Gamma^{M_1M_1'}_{MM'}=\Gamma$, $\Gamma_p\gtrsim\gamma^{\mu_1\mu_1'}_{\mu\mu'}=\gamma$, $\Gamma^{MM'}_{\mu\mu'}=0$. The relation between the rate constants, as adopted here, is typical for a number of experiments on diatomic molecules, cf., e.g., Refs. 7–10, 23, and 25. Let $\omega_{J'}=\omega_{J''}=\omega_S=0$, which indicates an absence of external magnetic field, and let the Stark shift be of zero value. Under such conditions there will be no coherence in the magnetic sublevel system, i.e., only diagonal elements of the density matrix differ from zero. It thus becomes possible to obtain $\varphi_{\mu\mu}$ for ground state J'' under conditions of stationary excitation, by applying the Wigner-Eckart

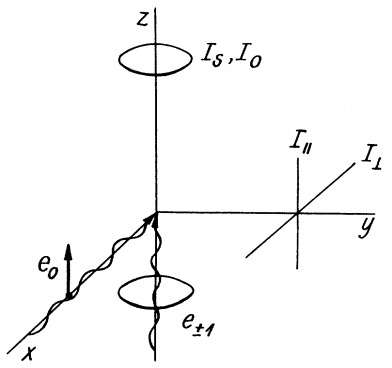

FIG. 2. "Standard" scheme of the geometry of plane polarized ($\mathbf{e}_0$) or circularly polarized ($\mathbf{e}_{\pm1}$) excitation. The intensities of the registered LIF are $I_\parallel, I_\perp$ or I_S, I_O, respectively.

theorem

$$\varphi_{\mu\mu}\propto 1/[1+\chi(C^{J'\mu+\eta}_{J''\mu1\eta})^2]\ . \tag{6}$$

Here $\chi=\Gamma_p/\gamma$ and $C^{J'\mu+\eta}_{J''\mu1\eta}$ are Klebsch-Gordan coefficients. Substituting (6) into the excited-state equation (1a), we have

$$f_{\mu+\eta\mu+\eta}\propto\varphi_{\mu\mu}(C^{J'\mu+\eta}_{J\mu1\eta})^2\ . \tag{7}$$

Since the magnetic sublevels of the excited state J' are incoherently populated, it is possible to represent the intensity of LIF with polarization $\mathbf{e}_f$ in the transition $J'\rightarrow J_1''$, cf. Fig. 1, and considering (4), in the following way:

$$I\propto\sum_\mu f_{\mu+\eta\mu+\eta}\sum_{\eta'}[(\mathbf{e}_f)_{\eta'}C^{J'\mu+\eta}_{J_1''\mu+\eta-\eta'1\eta'}]^2\ , \tag{8}$$

where $(\mathbf{e}_f)_{\eta'}$ are the cyclic components of the polarization vector in the LIF.

Let us apply standard geometry of observation, cf. Fig. 2. For plane-polarized excitation we have calculated the dependence of the degree of plane polarization $P=(I_\parallel-I_\perp)/(I_\parallel+I_\perp)$ and of anisotropy of polarization (or degree of alignment) $R=(I_\parallel-I_\perp)/(I_\parallel+2I_\perp)$ on parameter χ for all possible types of dipole transitions. For circularly polarized excitation we shall search for the χ dependence of circularity $C=(I_s-I_o)/(I_s+I_o)$, where I_s is the intensity of the LIF possessing the same circularity (i.e., polarized along the same circle) as the exciting radiation, and I_o possessing opposite circularity. Table I presents the obtained results. For the sake of comparison formulas are presented for weak excitation, when $\chi\rightarrow0$, as given in Refs. 26 and 27. Separate columns show limiting values for infinitely large angular momentum $J\rightarrow\infty$ and for very strong excitation $\chi\rightarrow\infty$. For certain types of molecular transitions, values P of the degree of polarization at arbitrary J values are presented in Refs. 6 and 28. An estimate of the effect of parameter χ on the polarization of LIF is frequently of principal importance; cf., e.g., Refs. 6, 7, and 29.

In solving the system of equations (1a) and (1b) in more

TABLE I. Expressions of polarization characteristics of radiation under conditions of optical pumping for various types of transition: $R(J)$, degree of anisotropy; $P(J)$, degree of plane polarization; $C(J)$, degree of circularity; J being the quantum number of the intial level, $P\uparrow, Q\uparrow, R\uparrow$ denotes absorption; $P\downarrow, Q\downarrow, R\downarrow$, emission. Summation is made over M from $M=-J$ to J.

				$\chi=0$		$\chi\neq 0$	$\chi\to\infty$	$\chi=0$	
	J''	J'	J_1''	$R(J)$	$R(\infty)$	$R(J)$	$R(J)$	$P(J)$	$P(\infty)$
$Q\uparrow Q\downarrow$	J	J	J	$\frac{(2J-1)(2J+3)}{10J(J+1)}$	$\frac{2}{5}$	$\frac{\sum \frac{M^2(3M^2-J^2-J)}{1+\chi M^2/[J(J+1)]}}{\sum \frac{M^2(J+1)2J}{1+\chi M^2/[J(J+1)]}}$	$\frac{1}{4J}$	$\frac{(2J-1)(2J+3)}{8J^2+8J-1}$	$\frac{1}{2}$
$R\uparrow R\downarrow$	J	$J+1$	J	$\frac{(J+2)(2J+5)}{10(J+1)(2J+1)}$	$\frac{1}{10}$	$\frac{\sum \frac{[(J+1)^2-M^2][(J+1)^2+(J+1)-3M^2]}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}}{\sum \frac{[(J+1)^2-M^2]2(J+1)(2J+1)}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}}$	$\frac{1}{2J+1}$	$\frac{(J+2)(2J+5)}{14J^2+23J+10}$	$\frac{1}{7}$
$P\uparrow P\downarrow$	J	$J-1$	J	$\frac{(J-1)(2J-3)}{10J(2J+1)}$	$\frac{1}{10}$	$\frac{\sum \frac{(J^2-M^2)(J^2-J-3M^2)}{1+\chi(J^2-M^2)/(2J^2+J)}}{\sum \frac{(J^2-M^2)(2J+1)2J}{1+\chi(J^2-M^2)/(2J^2+J)}}$	0	$\frac{(J-1)(2J-3)}{14J^2+5J+1}$	$\frac{1}{7}$
$R\uparrow P\downarrow$	J	$J+1$	$J+2$	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{\sum \frac{[(J+1)^2-M^2][(J+2)^2-(J+2)-3M^2]}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}}{\sum \frac{[(J+1)^2-M^2]2(J+2)[2(J+2)+1]}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}}$	$\frac{J+1}{2J^2+9J+10}$	$\frac{1}{7}$	$\frac{1}{7}$
$P\uparrow R\downarrow$	J	$J-1$	$J-2$	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{\sum \frac{(J^2-M^2)(J^2-J-3M^2)}{1+\chi(J^2-M^2)/(2J^2+J)}}{\sum \frac{(J^2-M^2)(4J^2-10J+6)}{1+\chi(J^2-M^2)/(2J^2+J)}}$	0	$\frac{1}{7}$	$\frac{1}{7}$
$Q\uparrow R\downarrow$	J	J	$J-1$	$-\frac{2J+3}{10J}$	$-\frac{1}{5}$	$\frac{\sum \frac{M^2(J^2+J-3M^2)}{1+\chi M^2/[J(J+1)]}}{\sum \frac{M^2 2J(2J-1)}{1+\chi M^2/[J(J+1)]}}$	$-\frac{J+1}{4J(2J-1)}$	$-\frac{2J+3}{6J-1}$	$-\frac{1}{3}$
$Q\uparrow P\downarrow$	J	J	$J+1$	$-\frac{2J-1}{10(J+1)}$	$-\frac{1}{5}$	$\frac{\sum \frac{M^2(J^2+J-3M^2)}{1+\chi M^2/[J(J+1)]}}{\sum \frac{M^2 2(2J^2+5J+3)}{1+\chi M^2/[J(J+1)]}}$	$-\frac{1}{4(2J+3)}$	$-\frac{2J-1}{6J+7}$	$-\frac{1}{3}$
$R\uparrow Q\downarrow$	J	$J+1$	$J+1$	$-\frac{2J+5}{10(J+1)}$	$-\frac{1}{5}$	$\frac{\sum \frac{(J+1+M)(J+1-M)(3M^2-J^2-3J-2)}{1+\chi(J+1+M)(J+1-M)/[(J+1)(2J+1)]}}{\sum \frac{(J+1+M)(J+1-M)2(J^2+3J+2)}{1+\chi(J+1+M)(J+1-M)/[(J+1)(2J+1)]}}$	$-\frac{1}{J+2}$	$-\frac{2J+5}{6J+5}$	$-\frac{1}{3}$
$P\uparrow Q\downarrow$	J	$J-1$	$J-1$	$-\frac{2J-3}{10J}$	$-\frac{1}{5}$	$\frac{\sum \frac{(J+M)(J-M)(3M^2-J^2+J)}{1+\chi(J+M)(J-M)/[J(2J+1)]}}{\sum \frac{(J+M)(J-M)2J(J-1)}{1+\chi(J+M)(J-M)/[J(2J+1)]}}$	0	$-\frac{2J-3}{6J+1}$	$-\frac{1}{3}$

general cases, it is necessary to use as much as possible the simplifications arising from symmetry properties of the problem. This procedure we are now going to apply.

III. EQUATION OF PM MOTION

For the solution of the system of equations (1a) and (1b) and for calculating LIF intensity (4) we shall further use the expansion of the density matrix over irreducible tensor operators T_Q^K:[24]

$$f_{MM'}=\sum_{K=0}^{2J'}\sum_{Q=-K}^{K} f_Q^K (T_Q^K)^*_{MM'}\,,$$
$$\varphi_{\mu\mu'}=\sum_{\kappa=0}^{2J''}\sum_{q=-\kappa}^{\kappa} \varphi_q^\kappa (T_q^\kappa)^*_{\mu\mu'}\,. \tag{9}$$

The expansion coefficients f_Q^K and φ_q^κ give us the PM values. Their physical meaning is as follows: f_0^0 and φ_0^0 are the populations of the corresponding levels, while

TABLE I. (*Continued*).

$\chi\neq 0$	$\chi\to\infty$	$\chi=0$		$\chi\neq 0$	$\chi\to\infty$
$P(J)$	$P(J)$	$C(J)$	$C(\infty)$	$C(J)$	$C(J)$
$\Sigma\frac{3M^4-J(J+1)M^2}{1+\chi M^2/[J(J+1)]}$ / $\Sigma\frac{M^4+J(J+1)M^2}{1+\chi M^2/[J(J+1)]}$	$\frac{3}{8J+1}$	$\frac{5}{8J^2+8J-1}$	0	$\Sigma\frac{(J^2+J-M^2-M)(M+1)}{1+\chi(J^2+J-M^2-M)/[2J(J+1)]}$ / $\Sigma\frac{(J^2+J-M^2-M)(J^2+J-M^2-2M-1)}{1+\chi(J^2+J-M^2-M)/[2J(J+1)]}$	$\frac{3}{4J^2+6J-1}$
$\Sigma\frac{[(J+1)^2-M^2][J^2+3J-3M^2+2]}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}$ / $\Sigma\frac{[(J+1)^2-M^2](3J^2+5J-M^2+2)}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}$	$\frac{3}{4J+3}$	$\frac{5(J+2)(2J+1)}{14J^2+23J+10}$	$\frac{5}{7}$	$\Sigma\frac{(2J+1)(M+1)(J+M+1)(J+M+2)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$ / $\Sigma\frac{[J(J+1)+M(M+2)+1](J+M+1)(J+M+2)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$	$\frac{3(2J+1)}{4J^2+4J+3}$
$\Sigma\frac{(J^2-M^2)(J^2-3M^2-J)}{1+\chi(J^2-M^2)/(2J^2+J)}$ / $\Sigma\frac{(J^2-M^2)(3J^2-M^2+J)}{1+\chi(J^2-M^2)/(2J^2+J)}$	0	$\frac{5(J-1)(2J+1)}{14J^2+5J+1}$	$\frac{5}{7}$	$\Sigma\frac{-(J-M-1)(J-M)(2J+1)(M+1)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$ / $\Sigma\frac{(J-M-1)(J-M)(J^2+J+M^2+2M+1)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$	0
$\Sigma\frac{[(J+1)^2-M^2](J^2+3J-3M^2+2)}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}$ / $\Sigma\frac{[(J+1)^2-M^2](3J^2+13J-M^2+14)}{1+\chi[(J+1)^2-M^2]/[(J+1)(2J+1)]}$	$\frac{3(J+1)}{4J^2+19J+21}$	$-\frac{5}{7}$	$-\frac{5}{7}$	$\Sigma\frac{-(J+M+1)(J+M+2)(M+1)(2J+5)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$ / $\Sigma\frac{(J+M+1)(J+M+2)(J^2+5J+M^2+2M+7)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$	$-\frac{3(2J+5)}{4J^2+16J+21}$
$\Sigma\frac{(J^2-M^2)(J^2-3M^2-J)}{1+\chi(J^2-M^2)/(2J^2+J)}$ / $\Sigma\frac{(J^2-M^2)[(3J-4)(J-1)-M^2]}{1+\chi(J^2-M^2)/(2J^2+J)}$	0	$-\frac{5}{7}$	$-\frac{5}{7}$	$\Sigma\frac{(J-M-1)(J-M)(2J-3)(M+1)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$ / $\Sigma\frac{(J-M-1)(J-M)(J^2-3J+M^2+2M+3)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$	0
$\Sigma\frac{M^2(J^2+J-3M^2)}{1+\chi M^2/[J(J+1)]}$ / $\Sigma\frac{M^2(3J^2-J-M^2)}{1+\chi M^2/[J(J+1)]}$	$-\frac{3(J+1)}{16J^2-9J-1}$	$\frac{5}{6J-1}$	0	$\Sigma\frac{(J-M)(J+M+1)(M+1)(2J-1)}{1+\chi(J-M)(J+M+1)/[2J(J+1)]}$ / $\Sigma\frac{(J-M)(J+M+1)(J^2-J+M^2+2M+1)}{1+\chi(J-M)(J+M+1)/[2J(J+1)]}$	$\frac{3}{4J-1}$
$\Sigma\frac{M^2(J^2+J-3M^2)}{1+\chi M^2/[J(J+1)]}$ / $\Sigma\frac{M^2(3J^2+7J-M^2+4)}{1+\chi M^2/[J(J+1)]}$	$-\frac{3(J+1)}{16J^2+39J+23}$	$-\frac{5}{6J+7}$	0	$\Sigma\frac{-(J-M)(J+M+1)(M+1)(2J+3)}{1+\chi(J-M)(J+M+1)/[2J(J+1)]}$ / $\Sigma\frac{(J-M)(J+M+1)(J^2+3J+M^2+2M+3)}{1+\chi(J-M)(J+M+1)/[2J(J+1)]}$	$-\frac{3(2J+3)}{8J^2+18J+13}$
$\Sigma\frac{(J+1+M)(J+1-M)(3M^2-J^2-3J-2)}{1+\chi(J+1+M)(J+1-M)/[(J+1)(2J+1)]}$ / $\Sigma\frac{(J+1+M)(J+1-M)(J^2+3J+M^2+2)}{1+\chi(J+1+M)(J+1-M)/[(J+1)(2J+1)]}$	$-\frac{3}{2J+3}$	$\frac{5}{6J+5}$	0	$\Sigma\frac{(J+M+1)(J+M+2)(M+1)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$ / $\Sigma\frac{(J+M+1)(J+M+2)(J^2+3J-M^2-2M+1)}{1+\chi(J+M+1)(J+M+2)/[2(J+1)(2J+1)]}$	$\frac{3}{2J^2+8J+3}$
$\Sigma\frac{(J+M)(J-M)(J-J^2+3M^2)}{1+\chi(J+M)(J-M)/[J(2J+1)]}$ / $\Sigma\frac{(J+M)(J-M)(J^2-J+M^2)}{1+\chi(J+M)(J-M)/[J(2J+1)]}$	0	$-\frac{5}{6J+1}$	0	$\Sigma\frac{(J-M-1)(J-M)(M+1)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$ / $\Sigma\frac{(J-M-1)(J-M)(J^2-J-M^2-2M-1)}{1+\chi(J-M-1)(J-M)/[2J(2J+1)]}$	0

other f_Q^1 and φ_q^1 coincide to within a factor accuracy with the mean values $\langle J'_Q\rangle$ or $\langle J''_q\rangle$ of the Q and q cyclic components of the full angular momentum of molecules in state J' or J''. For example, $\langle J'_Q\rangle=(-1)^Q\sqrt{J'(J'+1)}f_Q^1$. The PM values satisfy the relations $f_Q^K=(-1)^Q(f_{-Q}^K)^*$ and $\varphi_q^\kappa=(-1)^q(\varphi_{-q}^\kappa)^*$. Formation of PM of even range $K,\kappa=2,4,\ldots,$ is usually called alignment, and that of odd range $K,\kappa=1,3,\ldots,$ orientation.

The tensor operators are normalized, according to Ref. 24, in such a way that

$$(T_Q^K)_{MM'}=\frac{2K+1}{2J'+1}C_{J'MK-Q}^{J'M}\,. \tag{10}$$

A substantial advantage of such an expansion lies in the fact that the relaxation matrices $\Gamma_{MM'}^{M_1M'_1}$, $\Gamma_{\mu\mu'}^{MM'}$, and $\gamma_{\mu\mu'}^{\mu_1\mu'_1}$ are diagonal in many cases and do not depend on Q and q. This holds, in particular, in the present case under discussion, namely for isotropic collisions.

Let us now apply the expansion (9) to the system of equations (1a) and (1b): taking into account the orthogonality of the tensor operators, we obtain

$$\dot{f}^K_Q = \Gamma_p \sum_{X,\kappa} {}^K F^{X\kappa} \{\Phi^{(X)} \otimes \varphi^{(\kappa)}\}^K_Q + 2i\omega_S \frac{2J'+1}{2J''+1} \sum_{X,K'} {}^K A^{XK'}_{1-} \{\Phi^{(X)} \otimes f^{(K')}\}^K_Q$$
$$- \frac{2J'+1}{2J''+1} \sum_{XK'} {}^K A^{XK'}_{1+} \{\Phi^{(X)} \otimes f^{(K')}\}^K_Q - (\Gamma_K - iQ\omega_{J'}) f^K_Q \,, \tag{11a}$$

$$\dot{\varphi}^\kappa_q = -\Gamma_p \sum_{X,\kappa'} {}^\kappa A^{X\kappa'}_{+} \{\Phi^{(X)} \otimes \varphi^{(\kappa')}\}^\kappa_q + 2i\omega_s \sum_{X,\kappa} {}^\kappa A^{X\kappa'}_{-} \{\Phi^{(X)} \otimes \varphi^{(\kappa')}\}^\kappa_q$$
$$+ \Gamma_p \frac{2J'+1}{2J''+1} \sum_{X,K} {}^\kappa F^{XK}_1 \{\Phi^{(X)} \otimes f^{(K)}\}^\kappa_q - (\gamma_\kappa - iq\omega_{J''}) \varphi^\kappa_q + \Gamma_{J'J'} C_\kappa \delta_{K\kappa} \delta_{Qq} f^K_Q + \lambda^\kappa_q \delta_{\kappa 0} \delta_{q0} \,. \tag{11b}$$

The first term in the above equation describes absorption, the second describes the Stark frequency shift effect of the transition on the PM of the ground and excited states, and the third corresponds to stimulated light emission. The fourth term describes the relaxation of the PM at rates Γ_K, γ_κ and their external magnetic-field dependence.

The coefficients are

$${}^K F^{X\kappa} = \frac{(2J'+1)^{3/2}(2X+1)(2\kappa+1)}{(2J''+1)^{1/2}(2K+1)^{1/2}} (-1)^{X+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ \kappa & J'' & J'' \end{Bmatrix} , \tag{12}$$

$${}^\kappa A^{X\kappa'}_{\pm} = \frac{1 \pm (-1)^{\kappa+X+\kappa'}}{2} \frac{(2J'+1)(2X+1)(2\kappa'+1)}{(2\kappa+1)^{1/2}} (-1)^{J'+J''+\kappa'} \begin{Bmatrix} \kappa & X & \kappa' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J' \end{Bmatrix} , \tag{13}$$

$$C_\kappa = (-1)^{J'+J''+\kappa+1} (2J''+1)^{1/2} (2J'+1)^{1/2} \begin{Bmatrix} J'' & J'' & \kappa \\ J' & J' & 1 \end{Bmatrix} , \tag{14}$$

while the coefficients ${}^K A^{XK'}_{1\pm}$ and ${}^\kappa F^{XK}_1$ are obtained from ${}^\kappa A^{X\kappa'}_{\pm}$ and ${}^K F^{X\kappa}$ by interchanging J'' and J' in (12) and (13). The quantities inside the curly brackets are $6j$ and $9j$ symbols. The irreducible tensor product is defined as

$$\{\Phi^{(X)} \otimes f^{(K)}\}^\kappa_q = \sum_{\xi Q} C^{\kappa q}_{X\xi KQ} \Phi^X_\xi f^K_Q \,. \tag{15}$$

The Dyakonov tensor[24] Φ^X_ξ

$$\Phi^X_\xi(\mathbf{e}_a) = \frac{1}{(2X+1)^{1/2}} \sum_{q_1 q_2} (-1)^{q_2} e_{q_2} (e_{q_1})^* C^{X\xi}_{1q_1 1-q_2} \tag{16}$$

characterizes the polarization of the exciting light. Here e_{q_i} are the cyclic components of the polarization vector of the exciting light $\mathbf{e}_a$.

Let us now consider the problem of finding the tensor Φ^X_ξ in an explicit form at an arbitrary polarization of light. In similarity with Ref. 13, let us assume that excitation takes place along the **z** axis, cf. Fig. 3, and that the plane-polarized light beam with polarization vector $\mathbf{e}_a$ forming an angle ψ with the **x** axis is passed through a quarter-wave plate in which the "fast" axis **s** is parallel to the **x** axis. After passing through the quarter-wave plate the light becomes elliptically polarized and characterized by the tensor Φ^X_ξ with components $\Phi^0_0 = -1/\sqrt{3}$, $\Phi^1_0 = (1/\sqrt{6})\sin 2\psi$, $\Phi^1_{\pm 1} = 0$, $\Phi^2_0 = -1/\sqrt{30}$, $\Phi^2_{\pm 1} = 0$, $\Phi^2_{\pm 2} = (1/2\sqrt{5})\cos 2\psi$. The ellipticity parameters are determined by the choice of angle ψ. In special cases we have ψ equaling either 0 or $\pi/2$, and the light beam is plane polarized. In the case where $0 < \psi < \pi/2$, light is polarized along a left-hand ellipse; and in the case where $\pi/2 < \psi < \pi$, it is polarized along a right-hand ellipse, becoming left circular at $\psi = \pi/4$ and right circular at $\psi = 3\pi/4$.

For an arbitrary direction of excitation, determined by the spherical angles θ and φ and for the situation when the axis of the quarter-wave plate forms an angle α with the plane containing the exciting beam and the **z** axis, the tensor Φ^X_ξ can be found by rotating the physical system by the Euler angles α, θ, and φ. In the rotated system, Φ^X_ξ can be expressed through the components $\Phi^X_{\xi'}$ in the initial system by means of Wigner D matrices[19]

$$\Phi^X_\xi = \sum_{\xi'} (-1)^{\xi+\xi'} [D^X_{\xi\xi'}(\alpha,\theta,\varphi)]^* \Phi^X_{\xi'} \,. \tag{17}$$

Table II presents general expressions for Φ^X_ξ and values

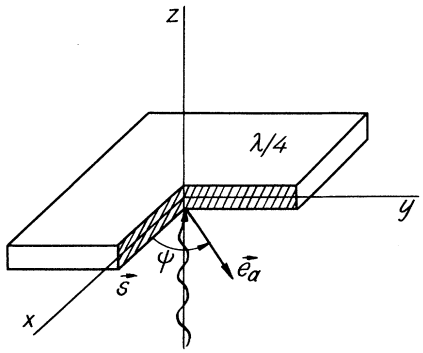

FIG. 3. Case of elliptically polarized excitation with application of a quarterwave plate with its "fast" axis **s**; $\mathbf{e}_a$ is the vector of the plane-polarized light falling on the plate.

TABLE II. General expressions and numerical values of the Dyakonov tensor Φ_ξ^X characterizing the state of polarization of light at a certain beam direction. For plane-polarized light the spherical angles θ,φ determine the direction of the polarization vector $\mathbf{e}_a$; in other cases, the direction of the light beam, α,θ,φ forming the Euler angles. Angle ψ is determined in Fig. 3.

	Polarization							
	Plane				Circular Right			
Φ_ξ^X	$\theta=0$	$\theta=\pi/2,\varphi=0$	$\theta=\pi/2,\varphi=\pi/2$		$\theta=0$	$\theta=\pi/2,\ \varphi=0$	$\theta=\pi/2,\ \varphi=\pi/2$	
Φ_0^0	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$
Φ_0^1	0	0	0	0	$\frac{1}{\sqrt{6}}$	0	0	$\frac{\cos\theta}{\sqrt{6}}$
Φ_1^1	0	0	0	0	0	$\frac{1}{2\sqrt{3}}$	$\frac{i}{2\sqrt{3}}$	$\sin\theta\frac{e^{i\varphi}}{2\sqrt{3}}$
Φ_{-1}^1	0	0	0	0	0	$-\frac{1}{2\sqrt{3}}$	$\frac{i}{2\sqrt{3}}$	$-\sin\theta\frac{e^{-i\varphi}}{2\sqrt{3}}$
Φ_0^2	$\frac{2}{\sqrt{30}}$	$-\frac{1}{\sqrt{30}}$	$-\frac{1}{\sqrt{30}}$	$\frac{3\cos^2\theta-1}{\sqrt{30}}$	$-\frac{1}{\sqrt{30}}$	$\frac{1}{2\sqrt{30}}$	$\frac{1}{2\sqrt{30}}$	$-\frac{3\cos^2\theta-1}{2\sqrt{30}}$
Φ_1^2	0	0	0	$\sin\theta\cos\theta\frac{e^{i\varphi}}{\sqrt{5}}$	0	0	0	$-\sin\theta\cos\theta\frac{e^{i\varphi}}{2\sqrt{5}}$
Φ_{-1}^2	0	0	0	$-\sin\theta\cos\theta\frac{e^{-i\varphi}}{\sqrt{5}}$	0	0	0	$\sin\theta\cos\theta\frac{e^{-i\varphi}}{2\sqrt{5}}$
Φ_2^2	0	$\frac{1}{2\sqrt{5}}$	$-\frac{1}{2\sqrt{5}}$	$\sin^2\theta\frac{e^{2i\varphi}}{2\sqrt{5}}$	0	$-\frac{1}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}$	$-\sin^2\theta\frac{e^{2i\varphi}}{4\sqrt{5}}$
Φ_{-2}^2	0	$\frac{1}{2\sqrt{5}}$	$-\frac{1}{2\sqrt{5}}$	$\sin^2\theta\frac{e^{-2i\varphi}}{2\sqrt{5}}$	0	$-\frac{1}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}$	$-\sin^2\theta\frac{e^{-2i\varphi}}{4\sqrt{5}}$

for the most frequently occurring special cases of the polarization of light. In the case of plane-polarized excitation the angles θ and φ in Table II characterize not the direction of propagation of the beam, as in all other cases, but that of the plane-polarization vector $\mathbf{e}_a$. The form of the tensor Φ_ξ^X for unpolarized light can be found in Ref. 24.

As may be seen in Table II, plane-polarized light can be described by a Dyakonov tensor Φ_ξ^X in which only even-range components differ from zero. In this case, if there is a coincidence between the center of the excitation line with the spectral transition frequency ω_0, which is equivalent to stating equality to zero of the value of ω_S in expression (3), only the PM φ_q^κ, f_Q^K of even range can be formed. This follows from the circumstance that for the coefficients ${}^KF^{X\kappa}$, ${}^\kappa F_1^{XK}$, ${}^KA_{1+}^{XK'}$, and ${}^\kappa A_+^{X\kappa'}$, as determined from formulas (12) and (13), the rule of even values of the sum of their upper indices must be valid. Hence, in the case of plane-polarized excitation, and in the absence of a dynamical Stark effect, only the alignment of the ensemble must take place.

For calculating the signals we observed, it is necessary to perform expansion over irreducible tensors also for LIF intensity (4) (Ref. 24)

$$I=I_0\sum_{K=0}^{2}(2K+1)\begin{Bmatrix}1 & 1 & K\\ J' & J' & J_1''\end{Bmatrix}\sum_{Q=-K}^{K}(-1)^Q f_Q^K\Phi_{-Q}^K, \quad (18)$$

where Φ_Q^K determines fluorescence polarization in this case. Thus, in the situation under consideration, only plane-polarized radiation will be observed, since $P\propto \mathrm{Re}f_2^2$.

In the presence of the dynamical Stark effect we have $\omega_s\neq 0$, i.e., in Eq. (11) there appear terms containing coefficients ${}^KA_{1-}^{XK'}$, ${}^\kappa A_-^{X\kappa'}$. They must, on the other hand, satisfy the requirement of odd values of the sum of the upper indices, cf. (13). This means that in the presence of an external magnetic field we have $\omega_{J'}\neq 0$, $\omega_{J''}\neq 0$, and in Eqs. (11), under the effect of plane-polarized light, in addition to the PM of even range, the PM of odd range are also formed. Hence, simultaneously with the alignment of the ensemble, orientation also takes place. It manifests itself in fluorescence through circularity $C\propto f_0^1$, differing from zero value if observed along the z axis, cf. Fig. 2. Such a transition of alignment into orientation is a purely quantum effect, since in the classical limit of high angular momentum values $J\to\infty$ the coefficients ${}^KA_{1-}^{XK'}$, ${}^\kappa A_-^{X\kappa'}$ assume zero value and vanish, as will be shown further (22).

IV. ASYMPTOTIC EQUATIONS OF PM MOTION

For molecular states large angular momentum values are typical.[30] On the one hand, this complicates the solution of the system of equations (11a) and (11b), since at large absorption rates Γ_p a large number of different PM's can be generated, $K\leq 2J'$, $\kappa\leq 2J''$. On the other hand, the addition coefficients of angular momentum become simpler, since asymptotic expressions may be used.[19] In particular,

TABLE II. (*Continued*).

Polarization				
Circular				
Left				
$\theta=0$	$\theta=\pi/2,\ \varphi=0$	$\theta=\pi/2,\ \varphi=\pi/2$		Elliptical
$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$
$-\frac{1}{\sqrt{6}}$	0	0	$-\frac{\cos\theta}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}\sin2\psi\cos\theta$
0	$-\frac{1}{2\sqrt{3}}$	$-\frac{i}{2\sqrt{3}}$	$-\sin\theta\frac{e^{i\varphi}}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}\sin2\psi\sin\theta e^{i\varphi}$
0	$\frac{1}{2\sqrt{3}}$	$-\frac{i}{2\sqrt{3}}$	$\sin\theta\frac{e^{-i\varphi}}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}\sin2\psi\sin\theta e^{-i\varphi}$
$-\frac{1}{\sqrt{30}}$	$\frac{1}{2\sqrt{30}}$	$\frac{1}{2\sqrt{30}}$	$-\frac{3\cos^2\theta-1}{2\sqrt{30}}$	$\frac{1}{2\sqrt{30}}(3\sin^2\theta\cos2\alpha\cos2\psi-2\cos^2\theta+1)$
0	0	0	$-\sin\theta\cos\theta\frac{e^{i\varphi}}{2\sqrt{5}}$	$-\frac{1}{2\sqrt{5}}[\cos2\psi\sin\theta(i\sin2\alpha-\cos2\alpha\cos\theta)+\sin\theta\cos\theta]e^{i\varphi}$
0	0	0	$\sin\theta\cos\theta\frac{e^{-i\varphi}}{2\sqrt{5}}$	$\frac{1}{2\sqrt{5}}[\cos2\psi\sin\theta(-i\sin2\alpha-\cos2\alpha\cos\theta)+\sin\theta\cos\theta]e^{-i\varphi}$
0	$-\frac{1}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}$	$-\sin^2\theta\frac{e^{2i\varphi}}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}[(1+\cos^2\theta)\cos2\psi\cos2\alpha+2i\cos\theta\cos2\psi\sin2\alpha-\sin^2\theta]e^{2i\varphi}$
0	$-\frac{1}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}$	$-\sin^2\theta\frac{e^{-2i\varphi}}{4\sqrt{5}}$	$\frac{1}{4\sqrt{5}}[(1+\cos^2\theta)\cos2\psi\cos2\alpha-2i\cos\theta\cos2\psi\sin2\alpha-\sin^2\theta]e^{-2i\varphi}$

$$\begin{Bmatrix} a & b & c \\ d+R & e+R & f+R \end{Bmatrix} \approx \frac{(-1)^{a+b+d+e}}{(2R)^{1/2}(2c+1)^{1/2}} C^{c\gamma}_{a\alpha b\beta} , \tag{19}$$

where $\alpha=f-e$, $\beta=d-f$, $\gamma=d-e$, $R\gg1$, and

$$\begin{Bmatrix} a & b+R & c+R \\ d & e+R & f+R \end{Bmatrix} \approx (-1)^{\varphi} \left[\frac{(a-b+c)!(a-e+f)!(c+d-e)!(-b+d+f)!}{(a+b-c)!(a+e-f)!(-c+d+e)!(b+d-f)!} \right]^{(1/2)\mathrm{sgn}(c+f-b-e)} \frac{(2R)^{-1-|b+e-c-f|}}{|b+e-c-f|} , \tag{20}$$

where

$$\varphi=a+d+\min(b+e,c+f), \quad \mathrm{sgn}X=\begin{cases} 1 & \text{when } X\geq 0 \\ -1 & \text{when } X<0 . \end{cases}$$

Using an expansion of $9j$ symbols into a $6j$-symbol series, we obtain

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} = \sum_y (-1)^{2y}(2y+1) \begin{Bmatrix} a & b & c \\ f & i & y \end{Bmatrix} \begin{Bmatrix} d & e & f \\ b & y & h \end{Bmatrix} \begin{Bmatrix} g & h & i \\ y & a & d \end{Bmatrix} , \tag{21}$$

which enables us to show that at a large-angular-momentum limit

$$\begin{aligned} &{}^{L_1}A^{L_2L_3}_{1-} = {}^{L_1}A^{L_2L_3}_{-} = 0, \quad C_\kappa = 1 , \\ &{}^{L_1}F^{L_2L_3} = {}^{L_1}F^{L_2L_3}_{1} = {}^{L_1}A^{L_2L_3}_{+} = {}^{L_1}A^{L_2L_3}_{1+} = {}^{L_1}S^{L_2L_3} = (-1)^{\Delta}\frac{(2L_2+1)^{1/2}(2L_3+1)^{1/2}}{(2L_1+1)^{1/2}} C^{L_20}_{1\Delta1-\Delta} C^{L_30}_{L_20L_10} , \end{aligned} \tag{22}$$

where $\Delta=J'-J''$, the system of equations (11a) and (11b) assumes the form

$$\dot{f}^K_Q=\Gamma_p\sum_{X,\kappa}{}^K S^{X\kappa}\{\Phi^{(X)}\otimes\varphi^{(\kappa)}\}^K_Q-\Gamma_p\sum_{X,K'}{}^K S^{XK'}\{\Phi^{(X)}\otimes f^{(K')}\}^K_Q-(\Gamma_K-iQ\omega_{J'})f^K_Q\ , \tag{23a}$$

$$\dot{\varphi}^\kappa_q=-\Gamma_P\sum_{X,\kappa'}{}^\kappa S^{X\kappa'}\{\Phi^{(X)}\otimes\varphi^{(\kappa')}\}^\kappa_q+\Gamma_P\sum_{X,K}{}^\kappa S^{XK}\{\Phi^{(X)}\otimes f^{(K)}\}^\kappa_q-(\gamma_\kappa-iq\omega_{J''})\varphi^\kappa_q+\Gamma_{J'J''}\delta_{K\kappa}\delta_{Qq}f^K_Q+\lambda^\kappa_q\delta_{\kappa0}\delta_{q0}\ . \tag{23b}$$

As can be seen, along with the simplification of coefficients in the asymptotic limit (23) the effect of the dynamic Stark effect on the produced PM's disappears.

The rate of approach of coefficients (19) and (20) (Ref. 19) to their limit with increasing R can be used for finding that the error in the values of the coefficients in Eqs. (23a) and (23b) is of the order J^{-1}. As a result of the asymptotic approximation, a number of coefficients in Eqs. (11a) and (11b) coincide [cf. (22)], which raises considerably the symmetry of the system of equations (23a) and (23b) and simplified their solution. If the equations are solved numerically, it may prove useful to use the dependence

$${}^{L_1}S^{L_2L_3}=(-1)^{L_2}\left[\frac{2L_3+1}{2L_1+1}\right]^{3/2}{}^{L_3}S^{L_2L_1}\ . \tag{24}$$

The expression for LIF, as obtained in a similar way, will be of the quite simple form, in comparison with (18),

$$I=I_0(-1)^{\Delta'}\sum_{K=0}^{2}(2K+1)^{1/2}C^{K0}_{1-\Delta'1\Delta'}\sum_{Q=-K}^{K}(-1)^Q f^K_Q\Phi^K_{-Q}, \tag{25}$$

where $\Delta'=J'-J''_1$.

V. EQUATIONS OF MOTION OF PROBABILITY DENSITY

Along with the equations of motion of the PM's, a classical analog of the density matrix, the probability density $\rho(\Omega,t),\Omega=\{\theta,\varphi\}$ is frequently used for the description of molecular processes. The physical meaning of the expression $\rho_\alpha(\Omega,t)d\Omega$ (where $\alpha=J'$ or J'' denotes its belonging to the ground or excited state) consists in the probability that at moment t the angular momentum **J** is positioned within the steric angle $d\Omega=\sin\theta\,d\theta\,d\varphi$. For the situation under discussion, Ducloy[20,31] employed differential equations of motion of probability density ρ_α in the analysis of the nonlinear interaction of resonance laser radiation with particles possessing a large angular momentum; a similar approach was concerned in Ref. 32. If we include in the system of equations from Ref. 20 the disorientating collisions which have not been considered there, then this system assumes the following form:

$$\begin{aligned}\dot{\rho}_{J'}(\Omega,t)=&\Gamma_p\int_{\Omega'}G'_2(\Omega,\Omega')\rho_{J''}(\Omega',t)d\Omega'\\&-\Gamma_pG_1(\Omega)\rho_{J'}(\Omega)\\&-\int_{\Omega'}\Gamma(\Omega,\Omega')\rho_{J'}(\Omega',t)d\Omega'-\omega_{J'}\frac{\partial}{\partial\varphi}\rho_{J'}(\Omega,t)\ ,\end{aligned} \tag{26a}$$

$$\begin{aligned}\dot{\rho}_{J''}(\Omega,t)=&-\Gamma_pG_2(\Omega)\rho_{J''}(\Omega,t)\\&+\Gamma_p\int_{\Omega'}G'_1(\Omega,\Omega')\rho_{J'}(\Omega',t)d\Omega'\\&-\int_{\Omega'}\gamma(\Omega,\Omega')\rho_{J''}(\Omega',t)d\Omega'-\omega_{J''}\frac{\partial}{\partial\varphi}\rho_{J''}(\Omega,t)\\&+\int_{\Omega'}\Gamma_{J'J''}(\Omega,\Omega')\rho_{J'}(\Omega',t)d\Omega'+\lambda_{J''}\ .\end{aligned} \tag{26b}$$

Here the terms that are proportional to $G_2(\Omega)$ and $G'_2(\Omega,\Omega')$ characterize absorption, while those proportional to $G_1(\Omega)$ and $G'_1(\Omega,\Omega')$ represent stimulated light emission. Functions $\Gamma(\Omega,\Omega')$ and $\gamma(\Omega,\Omega')$ describe the decay of states under the effect of radiational and collisional processes. The dependence on initial Ω' and final Ω orientations of momentum J shows that these same constants describe processes that do not change the full probability of finding the particle in the given state or, in other words, disorientating collisions. The constant ω_α, where $\alpha=J',J''$, is the Larmor precession frequency of the corresponding angular momentum in the external magnetic field, while the terms $\omega_\alpha(\partial/\partial\varphi)\rho_\alpha$ determine the rate of change of ρ_α as a result of this precession. The function $\Gamma_{J'J''}(\Omega,\Omega')$ describes the decay of level J' through the radiational transition $J'\to J''$. Finally, $\lambda_{J''}$, similar to the terms in (1b) and (11b), represents the rate of the population of level J'' in isotropic collision with the molecular thermostat.

Let us compare the asymptotic equations for PM's (23a), and (23b) and Eqs. (26a) and (26b) for probability density. To this purpose we expand $\rho_\alpha(\Omega,t)$ over spherical functions[33]

$$\rho_\alpha(\Omega,t)=(4\pi)^{-1/2}\sum_{K=0}^{\infty}\sum_{Q=-K}^{K}(2K+1)^{1/2}H_\alpha\rho^K_Q(t)Y^*_{KQ}(\Omega)\ . \tag{27}$$

The phase of functions $Y_{KQ}(\Omega)$ is chosen after Ref. 19, and the expansion is performed in such a way that the multipole moments ${}_\alpha\rho^K_Q$ are covariant with the spherical functions Y_{KQ} and are proportional to the mean value $\langle Y_{KQ}\rangle$ in state α. The physical meaning of ${}_\alpha\rho^0_0$ amounts to the full probability of finding the particle in state α and ${}_\alpha\rho^1_Q$ is proportional to the Q th cyclic component of the mean angular momentum of a separate molecule.

Let us carry out an expansion of equations [(26a) and (26b)] over spherical functions, and consider separately the summands entering into these equations. At the dipole transition in absorption and in stimulated emission it is possible to neglect the twist of J due to the absorption or emission of a photon by the molecule, owing to the negligible value of the photon's angular momentum, as compared to that of the molecule. This means that

$$G'_1(\Omega,\Omega')=G_1(\Omega)\delta(\Omega-\Omega')=G(\Omega)$$

and

$$G_2'(\Omega,\Omega')=G_2(\Omega)\delta(\Omega-\Omega')=G(\Omega)\ ,$$

and

$$\Gamma_{J'J''}(\Omega,\Omega')=\Gamma_{J'J''}(\Omega)\delta(\Omega-\Omega')\ ;$$

here $\delta(\Omega-\Omega')$ is a Dirac delta function and, according to Refs. 20 and 31, the function describing the angular dependence of absorption and emission can be calculated as

$$G(\Omega)=|\mathbf{e}_a\mathbf{n}_{J''-J'}|^2\ , \tag{28}$$

where $\mathbf{n}_{J''-J'}$ is a unit vector directed along the dipole moment of the molecule transition. For a transition of the Q type, $\mathbf{n}_{J''-J'}$ is directed along $\mathbf{J}$, while for P-or R-type transitions it rotates either clockwise or anticlockwise looking from the end of $\mathbf{J}$. In laboratory coordinates we have

$$G(\Omega)=\left|\sum_Q(-1)^Q(\mathbf{e}_a)_{-Q}D^{(1)}_{QJ''-J'}(\varphi,\theta,0)\right|^2\ . \tag{29}$$

If we consider relaxation terms containing $\Gamma(\Omega,\Omega')$ and $\gamma(\Omega,\Omega')$, we notice that at isotropic collision these functions are dependent on angle Θ between the direction of vector $\mathbf{J}$ before the collision (determined by angles $\Omega'=\{\theta',\varphi'\}$), and after it (determined by angles $\Omega=\{\theta,\varphi\}$), but that they do not depend on the concrete values of these angles. It is then convenient to expand functions $\Gamma(\Theta)$ and $\gamma(\Theta)$ over bipolar harmonics.[19] For instance,

$$\gamma(\Theta)=\sum_{K=0}^{\infty}\gamma_K\sum_{Q=-K}^{K}Y_{KQ}(\Omega')Y^*_{KQ}(\Omega)\ . \tag{30}$$

Using formulas (28) and (29) and the well-known dependence[19]

$$\int Y_{l_1m_1}(\Omega)Y^*_{l_2m_2}(\Omega)Y^*_{l_3m_3}(\Omega)d\Omega=\frac{(2l_2+1)^{1/2}(2l_3+1)^{1/2}}{(4\pi)^{1/2}(2l_1+1)^{1/2}}C^{l_10}_{l_20l_30}C^{l_1m_1}_{l_2m_2l_3m_3}\ , \tag{31}$$

it is possible to obtain a system of equations for the coefficients of multipole expansion of the initial equations (26a) and (26b),

$$\dot{{}_{J'}\rho}{}^K_Q=\Gamma_P\sum_{X,K'}\frac{(2X+1)(2K'+1)}{4\pi(2K+1)}C^{K0}_{X0K'0}(\{G^{(X)}\otimes{}_{J''}\rho^{(K')}\}^K_Q-\{G^{(X)}\otimes{}_{J'}\rho^{(K')}\}^K_Q)-(\Gamma_K-i\omega_{J'}Q)_{J'}\rho^K_Q\ , \tag{32a}$$

$$\dot{{}_{J''}\rho}{}^K_Q=-\Gamma_p\sum_{X,K'}\frac{(2X+1)(2K'+1)}{4\pi(2K+1)}C^{K0}_{X0K'0}(\{G^{(X)}\otimes{}_{J''}\rho^{(K')}\}^K_Q-\{G^{(X)}\otimes{}_{J'}\rho^{(K')}\}^K_Q) \tag{32b}$$

$$-(\gamma_\kappa-i\omega_{J''}Q)_{J''}\rho^K_Q+\Gamma_{J'J''\,J'}\rho^K_Q+\lambda^K_Q\delta_{K0}\delta_{Q0}\ .$$

These equations, both in form and content, are very close to the asymptotic equation for PM's (23a) and (23b). Their basic difference consists in the description of the exciting light. The multipole moments G^X_ξ, as introduced in (32a) and (32b), are obtained as a result of multipole expansion of $G(\Omega)$ similarly to (27), while the tensor Φ^X_ξ is used in (23a) and (23b) for describing the exciting radiation. Both magnitudes are connected in the following way:

$$G^X_\xi=(-1)^\Delta\frac{1}{(2X+1)^{1/2}}C^{X0}_{1\Delta1-\Delta}\Phi^X_\xi\ . \tag{33}$$

If the coefficients in the multipole expansion of ${}_{J'}\rho^K_Q$ are known, it is possible to calculate the intensity of LIF in the $J'\rightarrow J_1''$ transition

$$I=I_0\int_\Omega{}_{J'}\rho(\Omega)G(\Omega)d\Omega=I_0(4\pi)^{-1/2}\sum_{K=0}^{2}(2K+1)\sum_{Q=-K}^{K}(-1)^Q{}_{J'}\rho^K_QG^K_{-Q}\ , \tag{34}$$

where, in this case, $G(\Omega)$ determines the angular dependence of the radiational transition and may be calculated after (29), if the index $J''-J'$ in the Wiegner D function is replaced by $J'-J_1''$, cf. Fig. 1.

Since the magnitudes ${}_\alpha\rho^K_Q$ represent multipole moments in the continuous distribution $\rho_\alpha(\Omega)$, the latter may be depicted graphically[34] for a given set of multipole moments ${}_\alpha\rho^K_Q$. Thus, for instance, Fig. 4 shows isometric projections of the function $\rho_\alpha(\Omega)$ in three cases, when the spatial distribution of the angular momentum is described by a minimal number of multipoles (or, which is equivalent, polarization moments). This figure illustrates rather clearly the physical meaning of PM's in the classical limit of a large angular momentum. Figure 4(a) corresponds to a situation when, as a rule, the ensemble is said to lack coherence, i.e., $Q=0$. This function is symmetric with respect to rotation by any angle around the z axis. In the other two cases, Figs. 4(b) and 4(c), coherence is produced in the ensemble, i.e. $Q\neq0$ (in the quantum approach $Q=\Delta M_J$ shows between which magnetic sublevels coherence has been produced). For distributions of this kind the z axis forms an axis of Qth-order symmetry. This result means that, in the case of the classical approach to a particle ensemble, coherence may be treated from the pont of view of the symmetry of the probability density $\rho_\alpha(\Omega)$. Such a procedure is useful for the visual interpretation of experimental results and calculations performed in the PM approach.

It ought to be noted that the statement about the presence or absence of coherence in a particle ensemble is

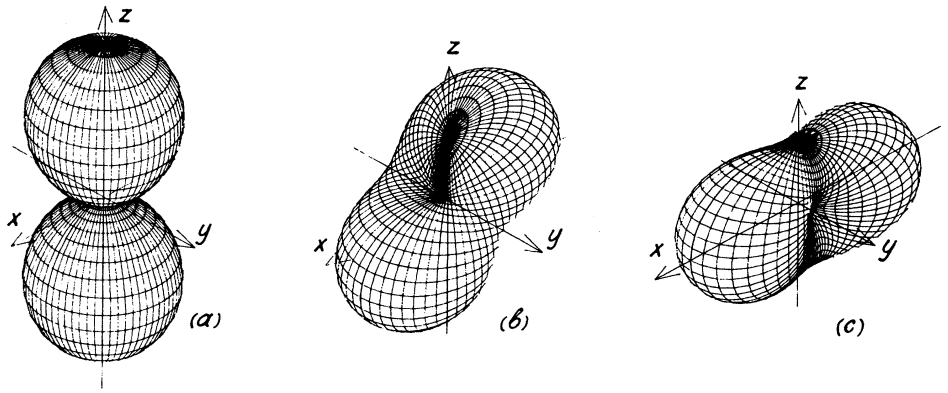

FIG. 4. Isometric projections of functions $\rho_\alpha(\Omega)$ which characterize the spatial distribution of angular moments of a state at a given set of expansion coefficient values ${}_\alpha\rho_Q^K$ in expression (27). (a) Values ${}_\alpha\rho_0^0=1$, ${}_\alpha\rho_0^2=0,3$. (b) ${}_\alpha\rho_0^0=1$, ${}_\alpha\rho_1^2=-{}_\alpha\rho_{-1}^2=0,15$. (c) ${}_\alpha\rho_0^0=1$, ${}_\alpha\rho_2^2={}_\alpha\rho_{-2}^2=0,15$. The remaining ${}_\alpha\rho_Q^K$ values equal zero.

rather conditional in a number of cases and depends on the choice of the coordinate system. Thus, in Fig. 5(a), a distribution of angular momenta of a molecule is shown at excitation by light which is plane polarized along the **y** axis. A Q type of absorption is considered, and it is assumed that $\Gamma_p \ll \Gamma_K = \Gamma_1$ $\gamma_\kappa = \gamma$, $\Gamma_{J'J''} = \omega_{J'} = \omega_{J''} = 0$. The **z** axis is a second-order axis of symmetry in this case and, accordingly, we have coherence in the system between $\Delta M_{J'} = Q = 2$.

Figure 5(b) shows a distribution, as obtained by looking from the end of the **y** axis. It may be seen at such a turn of the coordinate system, if we wish the **z** axis to coincide with the initial position of the **y** axis after transformation, that the distribution of angular momentum must be symmetrical with respect to the **z** axis, i.e., there will be no coherence in the ensemble.

Figure 5(c) shows the same distribution of angular momentum at switching on an external magnetic field. In

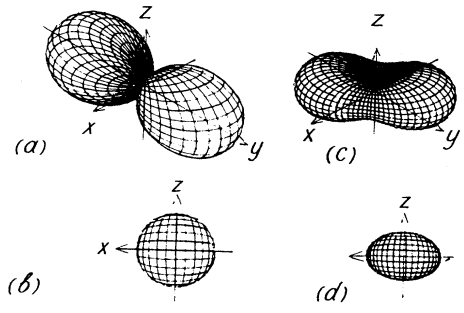

FIG. 5. Distribution of angular momenta J at $Q\uparrow$ excitation by light plane polarized along the y axis. (a) Isometric projection of distribution in absence of external magnetic field. (b) Same as (a), viewing from end of y axis. (c) Isometric projection of distribution in the presence of the external magnetic field for the ratio between the precession frequency and the relaxation rate equaling $\omega_{J'}/\Gamma = 0,5$. (d) View of distribution, case (c) from the end of the symmetry axis in the xy plane.

calculating the distribution of angular momentum the ratio $\omega_{J'}/\Gamma = 0,5$ is assumed. The other parameters are the same as in the first case. This time, looking at the distribution from the end of the symmetry axis positioned in the xy plane, cf. Fig. 5(d), it may be seen that this axis is a second-order symmetry axis. Hence, if the **z** axis is positioned along the direction under observation, second-order coherence remains all the same in the system of molecular particles. The results obtained are in good agreement with those of quantum-mechanical analysis of the concept of coherence.[35]

In conclusion, a few words ought to be said about the possibility of solving the system of equations (23a) and (23b) with sufficient accuracy that describes the results of experimental investigations. The main difficulties here are due to the existence of an infinite number of interconnected equations in the $J \to \infty$ limit. However, in calculating LIF the signal is under the direct influence of only the PM's f_Q^K of the excited state with range $K \leq 2$. These are directly linked with the PM's of the ground state φ_q^κ of range $\kappa \leq 4$ by the radiational field, as may be seen from Eq. (23a), for which the triangle rule must be valid for the indices of coefficient ${}^K S^{\chi\kappa}$. The PM's of higher range affect the LIF signal only indirectly. Therefore, as experienced in the case of solving, with the aid of a computer, the system (23a) and (23b),[36] it is sufficient for $\Gamma_p/\Gamma_K, \Gamma_p/\gamma_\kappa \leq 10$ to take into account the PM's φ_q^κ and f_Q^K of range $K, \kappa \leq 10$ for achieving a relative accurancy of LIF intensity of the order of 10^{-3}. The system (23a) and (23b) generally contains 242 equations, in this case.

The above-mentioned statement is illustrated by Figs. 6 and 7, which present the PM's φ_0^κ of various range κ as dependent on the parameter $\chi = \Gamma_p/\gamma$, which determines nonlinearity, for the case $\Gamma_K = \Gamma \gg \Gamma_p$, $\Gamma_{J'J''} = \omega_{J'} = \omega_{J''} = 0$, $\gamma_\kappa = \gamma$. Applying plane-polarized light, the **z** axis was chosen along the $\mathbf{e}_a$ vector, while in the case of circularly polarized light, it was chosen along the direction of propagation of the light beam. The figures demonstrate that the absolute value of the PM's decreases with an increase of range κ, which permits one to use a relatively small number of PM's in the calculation.

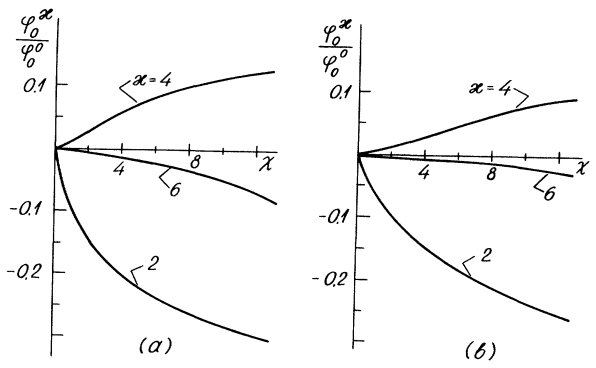

FIG. 6. Relative value of ground-state PM $\varphi_0^\kappa/\varphi_0^0$, $\kappa=2$, 4, and 6 at optical pumping by plane-polarized light, as dependent on pumping parameter $\chi=\Gamma_p/\gamma$. (a) $Q\uparrow$ transition type; (b) $P\uparrow, R\uparrow$ transition types.

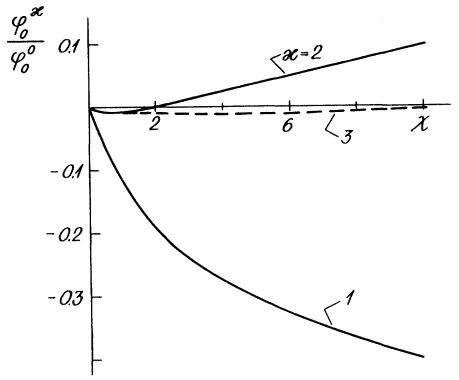

FIG. 7. Relative value of ground-state PM $\varphi_0^\kappa/\varphi_0^0$, $\kappa=3,2$, and 1 at optical pumping by circularly polarized light for $P\uparrow, R\uparrow$ transition type.

VI. CONCLUSION

Optical pumping (alignment, orientation) of a certain initial (lower) level of a molecular electronic ground state by excitation of laser radiation of wide spectral range is by no means anything extraordinary or "exotic." It is rather a situation sufficiently frequently observed in reality. To a smaller or larger extent it generally takes place in absorption of laser radiation by diatomic molecules. A description of the process has been given for arbitrary angular momentum values for a model which accounts for all radiational processes, interaction with an external magnetic field, dynamical Stark effect, as well as relaxation processes in relaxation constant approximation. It is assumed, at the same time, that there is an absence of dependence of absorption on coordinates and velocities of particles interacting with light. In other words, the relaxation process, in the course of motion through the exciting laser beam and in collisions can be described by a single constant of the summary process. A situation, when this cannot be done, has been analyzed in Refs. 37 and 38 by us. Another assumption consists in the concept of the existence of a "thermostat" of states in the vicinity of the emptied level. These states have not undergone optical pumping, and "supply" only the population to the pumped level in isotropic collisions (Fig. 1).

In the absence of an external magnetic field changing the symmetry of the system, the description of polarization characteristics of the system, such as the anisotropy of LIF from the optically pumped level, is sufficiently simply (for any J value) performed in the JM representation. It may be seen from Table I, the way in which the polarizational characteristics of such LIF (e.g., in the transition $J'\rightarrow J_1''$, Fig. 1) depend on the optical pumping parameter at various polarizations of the exciting light.

The general case of the presence of coherence in a set of particles is most simply described in terms of polarization moments. Such a description may be performed, in principle, for any, including arbitrarily large, values of angular momentum J. In a number of cases this is necessary, despite the highly complex nature of the equations at $J\gg 1$. Thus, if a high accuracy of absolute values is required in the calculation of polarizational characteristics of radiation, it proves impossible to pass over to the asymptotic limit, owing to a low convergence of certain types of transition, even at values of $J\approx 50$. This can also not be done in the calculation of such specifically quantum phenomena as the dynamic Stark effect. Nevertheless, in a wide range of interference signals (level crossing, quantum beats, etc.) and for typical molecular states it is fully sufficient to give a description using asymptotic formulas for coefficients of moment addition. While preserving all the advantages of a clear interpretation of effects, the asymptotic approach proves to be considerably simpler. It has been found (Figs. 6 and 7) that one of the peculiarities of the situation under study consists in the fact that, in the ground state, PM's are "readily" formed in the range higher than 2, even at relatively small pumping parameters.

On the other hand, in such a "classical" limit as $J\rightarrow\infty$, a quantum-mechanical description, according to the correspondence principle, may be successfully replaced by the classical one, in terms of probability density and expanding over multipole moments. Both approaches being equivalent [cf. Eqs. (23) and (32)], in full accordance with the correspondence principle, we obtain a definite advantage of imaginability. This makes it possible to "visualize" the manifestation of multipole moments of various ranges in the distribution of angular momentum (Fig. 4), as well as to clarify, the manner in which coherence and symmetry are connected, cf. Fig. 5.

[1]A. Kastler, J. Phys. Radium. **11**, 225 (1950).
[2]J. Brossel, A. Kastler and J. Winter, J. Phys. Radium. **13**, 668 (1952).
[3]W. Happer, Rev. Mod. Phys. **44**, 169 (1972).
[4]G. W. Series, Contemp. Phys. **22**, 487 (1981).
[5]P. R. Berman, Ann. Phys. (Paris) **10**, 984 (1985).
[6]R. E. Drullinger and R. N. Zare, J. Chem. Phys. **51**, 5532 (1969).
[7]R. E. Drullinger and R. N. Zare, J. Chem. Phys. **59**, 4225 (1973).
[8]R. S. Ferber, O. A. Schmit, and M. Ya. Tamanis, Chem. Phys. Lett. **61**, 441 (1979).
[9]R. S. Ferber, A. I. Okunevich, O. A. Schmit, and M. Ya. Tamanis, Chem. Phys. Lett. **90**, 476 (1982).
[10]M. P. Auzin'sh, R. S. Ferber, and M. Ya. Tamanis, Pis'ma Zh. Eksp. Teor. Fiz. **42**, 132 (1985) [JETP Lett. **42**, 160 (1985)]; Zh. Eksp. Teor. Fiz. **90**, 1182 (1986) [Sov. Phys.—JETP **63**, 688 (1986)].
[11]S. D. Rosner, R. A. Holt, and T. D. Gaily, Phys. Rev. Lett. **35**, 758 (1976).
[12]C. H. Greene and R. N. Zare, J. Chem. Phys. **78**, 6741 (1983).
[13]A. C. Kummel, G. O. Sitz, and R. N. Zare, J. Chem. Phys. **88**, 7357 (1988).
[14]J. C. Waldeck, A. C. Kummel, G. O. Sitz, and R. N. Zare, J. Chem. Phys. **90**, 4112 (1989).
[15]C. Cohen-Tannoudji, Ann. Phys. (Paris) **7**, 427 (1962).
[16]M. Ducloy, Phys. Rev. A **8**, 1844 (1973); **9**, 1319 (1974).
[17]E. N. Kotlikov and V. A. Kondratyeva, Opt. Spektrosk. **48**, 667 (1980) [Opt. Spectrosc. (U.S.S.R.) **48**, 367 (1980)].
[18]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, London, 1955).
[19]D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
[20]M. Ducloy, J. Phys. B **9**, 357 (1976).
[21]D. A. Case, G. M. McClelland, and D. R. Herschbach, Mol. Phys. **35**, 541 (1978).
[22]A. M. Bonch-Bruyevich and V. A. Hodovoy, Usp. Fiz. Nauk **93**, 71 (1967) [Sov. Phys.—Usp. **10**, 637 (1967)].
[23]C. Ottinger and M. Schröder, Chem. Phys. **45**, 3533 (1980).
[24]M. I. Dyakonov, Zh. Eksp. Teor. Fiz. **47**, 2213 (1964) [Sov. Phys.—JETP **20**, 1484 (1965)].
[25]R. Feinberg, R. E. Teets, J. Rubbmark, and A. L. Schawlow, J. Chem. Phys. **66**, 4330 (1977).
[26]P. P. Feofilov, *The Physical Basis of Polarized Emission* (Consultants Bureau, New York, 1961).
[27]R. N. Zare, *Angular Momentum* (Wiley-Interscience, New York, 1988).
[28]M. P. Auzin'sh, Opt. Spektrok. **63**, 1220 (1987) [Opt. Spectrosc. (U.S.S.R.) **63**, 721 (1987)].
[29]R. S. Ferber, Izv. Akad. Nauk SSSR, Ser. Fiz. **43**, 419 (1979).
[30]G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1957).
[31]M. Ducloy, J. Phys. (Paris) **36**, 927 (1975).
[32]K. A. Nasyrov and A. M. Shalagin, Zh. Eksp. Teor. Fiz. **81**, 1649 (1981) [Sov. Phys.—JETP **54**, 877 (1981)].
[33]M. P. Auzin'sh, R. S. Ferber, Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tehn., **3**, 3 (1985).
[34]M. P. Auzin'sh, Opt. Spektrosk. **60**, 406 (1986) [Opt. Spektrosc. (U.S.S.R.) **60**, 248 (1986)].
[35]K. Blum, *Density Matrix. Theory and Applications* (Plenum, New York, 1981).
[36]M. P. Auzin'sh, Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tehn. **1**, 9 (1984).
[37]M. P. Auzin'sh, R. S. Ferber, and I. Ya. Pirags, J. Phys. B **16**, 2759 (1983).
[38]M. P. Auzin'sh, M. Ya. Tamanis, R. S. Ferber, and Ya. A. Harya, Opt. Spektrosk. **67**, 1274 (1989).