

# Optical polarization of diatomic molecules

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Originally, he says, man was round, his back and sides forming a circle. Hermann Weyl, "Symmetry" (on Plato's Dialogue "Symposium"). The evolution of polarization (alignment and orientation) of angular momenta of diatomic molecules both in the ground and excited states upon absorption of light is examined. The effect of external factors—magnetic field and collisions—on this polarization is investigated. Interference effects (level crossing, quantum beats, beat resonance) and the possibilities of employing them to determine magnetic and relaxation characteristics of individual vibration-rotation levels are analyzed. A classical description of phenomena is given in terms of distribution of angular momenta, including the use of isometric projections of the distribution being formed. Equations are given that describe the interaction of intense laser radiation with an ensemble of molecules in the gas phase. Other mechanisms are presented for the evolution of angular momenta for the ground electron state of diatomic molecules.

## 1. INTRODUCTION

It is likely that an understanding of the generation of an anisotropic distribution of the angular momenta of atoms in light absorption was ultimately formulated at the same time as the understanding of the precession of this distribution in an external field. Direct consequence of this precession is the magnetic depolarization of resonance fluorescence, or the Hanle effect, which was detected and interpreted in a classical model in a work by Hanle in 1924.<sup>1</sup> In that and subsequent papers, only the excited state was discussed. In 1950, the paper of Kastler appeared.<sup>2</sup> This article proposed that an anisotropy of atomic angular momenta in the ground state could be created using polarized optical radiation. In the language of quantum concepts, one could, in the simplest case, "pump" atoms into a specific magnetic sublevel. Kastler called the entire process "optical pumping" ("pompage optique") to stress the decisive role of optical radiation as a "pump." In practice one also needs a favorable "play" between radiative and relaxation processes, as a result of which unexcited atoms, for example, alkali metals, acquire a dominant orientation of electron spins. Here we cannot refrain from again presenting the "classical" scheme, Fig. 1, which illustrates a simple and elegant idea of the method using the example of a hypothetical alkali atom without a nuclear spin and without relaxation in the ground state. It is clear that circularly polarized radiation, in the final analysis, "pumps" atoms in the ground electronic state to a magnetic sublevel with  $m_j = +1/2$ ; that is, the spin of the electron is oriented along the light beam.

The optical pumping method, combined with the magnetic resonance method, became a standard instrument for the study of the intervals of fine and hyperfine structure and relaxation processes, which are the basis of supersensitive quantum magnetometers and frequency standards. A large number of original articles, surveys, and monographs have been published on variations on the methods, including laser methods. The maturity of this direction of research is indicated by papers devoted to the anniversaries of the method.<sup>3</sup> International Kastler symposia have become a tradition; see, for example, the materials in Refs. 4 and 5, and in the USSR, the all-union seminars at the A. F. Ioffe Physico-Technical Institute of the USSR Academy of Sciences.<sup>6</sup> More than

once have surveys been published on the optical pumping of atoms. The first of these surveys were Refs. 7 and 8, and some surveys have appeared in this journal. The material is also presented in Ref. 9.

Although the quantitative characteristics of the polarized radiation of molecules was classically interpreted already in 1923 in the work of Vavilov and Levshin,<sup>10</sup> the Hanle effect for the fluorescence of diatomic molecules was recorded<sup>14</sup> only much later, in 1969, in sodium dimers  $\text{Na}_2$  ( $B^1\Pi_u$ ). The physical reason for the Hanle effect, which is the result of the precession of the magnetic and associated angular momenta around an applied magnetic field, is the same as for atomic states. However, there are a number of differences of principle for molecules. First, the electron magnetic moment  $\mu$ , which is of the same order of magnitude as that of atoms, is almost perpendicular to the angular momentum  $J$ . The angular momentum is mainly defined by the rotation, and has a large value. Thus, the ratio of the projection  $\mu_j$  to  $J$  is, as a rule, much smaller than the Bohr magneton  $\mu_0$ ; that is, the Landé factor is much less than unity. Thus, the Zeeman splitting is extremely small, and observation of the Hanle effect requires large magnetic fields. Second, the large values of  $J$  correspond to a large number ( $2J + 1$ ) of components of Zeeman splitting. This makes it possible to consider the projection of the angular momentum on the  $z$  axis continuous. It is significant that it was also in 1969 that Demtröder, Zare, *et al.* completed a series of studies<sup>11,13,14</sup> which laid the foundation of the method of laser-induced fluorescence for diatomic molecules, in which the Hanle method is applied<sup>14</sup> (in modern

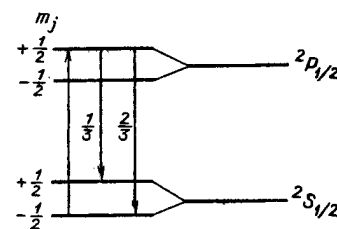


FIG. 1. Schematic of the optical orientation of the  $2S_{1/2}$  state; numbers indicate the relative probabilities of radiative transitions.

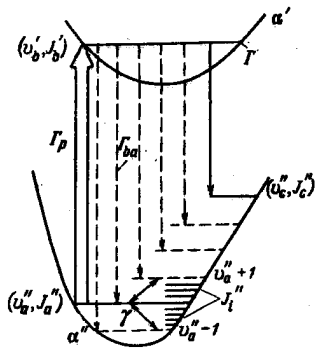


FIG. 2. Schematic of transitions of laser-induced fluorescence.  $\Gamma_p$  is the rate of absorption,  $\Gamma$ ,  $\gamma$  are the relaxation rates.

terms, the intersection of the Zeeman sublevels in a zero magnetic field<sup>15,16</sup>). Finally, it was demonstrated<sup>11,12</sup> that it was possible to use laser optical absorption to create an anisotropic distribution of angular momenta not only in an excited (upper) state, but also in an initial (lower) state. This method can also be called optical pumping, although the schematic for its implementation differs from the Kastler schematic. In Fig. 1 we have a closed absorption-radiation cycle for atoms; for molecules, however, the simplest approximation is the open cycle,<sup>17,18</sup> shown in Fig. 2. In this case, due to spontaneous radiation due to the large number of possible transitions to various oscillation levels  $u''_i$ , only a small number of molecules return to the initial state  $a$  in the resonance progression of fluorescence. As a result, level  $a$ , which has fixed vibration-rotation numbers,  $u''_a, J''_a$ , has a population density which differs from an equilibrium population density (it is smaller). But for us what is most important is that, due to the angular dependence of absorption in the excitation of polarized or even simply directed light, an anisotropic spatial distribution of angular momenta is created. It is this distribution, its various manifestations, and its use that are the subject of this article.

A few words on terminology. In foreign publications, one speaks of "optical pumping" (Refs. 2-5, 7, 8, 11, and 12). In domestic literature, this is not totally unambiguous, since the term "optical pumping" is more frequently used for laser media in the sense of optical excitation; thus the term "optical orientation" is used.<sup>6,19</sup> However, strictly speaking, this definition does not encompass the effect of linearly polarized light or directed unpolarized light when there is no dominant orientation of the angular momenta of the ensemble, that is, the orientation vector. An axis of symmetry is created (the  $z$  axis in Figs. 4a and 4b) along which the average angular momenta of the ensemble are greater (see Fig. 4a) or less (see Fig. 4b) than they are in the perpendicular plane. This ordered distribution of angular momenta is called "optical alignment."<sup>20</sup> The alignment may be positive (see Fig. 4a) or negative (see Fig. 4b), and is characterized by a quadrupole moment (the role of higher order moments will be discussed below). Thus, instead of optical pumping, one can speak of "optical alignment and orientation."<sup>20</sup> The search for a single term which summarizes the examined cases led us to the term "optical polarization" (referring to the angular momenta of the ensemble of particles, and not the light beam) which is used in the title of this article. Also, not neglecting the international tradition, we reserve the

right to use the term "optical pumping" in the sense of Kastler and Zare.

In other terms, this phenomenon involves the creation of a nonequilibrium population density in the Zeeman sublevels.<sup>21</sup> From this it is clear that the fundamental role is played by the external magnetic field, to which a large part of the material given here is devoted.

The main subject of this survey is diatomic molecules in the ground electronic state. The basic method of detection is intensity, polarization, and the kinetics of fluorescence, which is stimulated either by the pumping light itself or a probe beam. We note that in the first case the signal is nonlinear, and in the second, it infers excitation which is linear in absorption by a weak light flux. Recently, other methods of detection have become more popular. These methods are associated with the recording of absorption caused by induced anisotropy of molecular gas, and methods based on two- and  $n$ -photon resonantly amplified ionization with subsequent recording of the ions.

The main approach to the description of the phenomena is a classical one based on the probability density of the distribution of angular momenta. The following considerations are made here. First, frequently we speak of states with a rather large angular momentum with a quantum number of the order of 10-100, so the classical approach should be totally applicable. Second, it has the advantage of clarity, and in the majority of cases, it is simpler. Finally, it is interesting to trace the transition of quantum concepts and terms, such as the coherence between Zeeman sublevels, into classical ones, or in essence, how the correspondence principle is satisfied. One should note the recent heightened interest in classical concepts, for example, the application to the superposition of the Rydberg states of atoms in Refs. 22 and 23, which demonstrated clear confirmations of the orbital rotation of the electron.

For completeness, we present the quantum mechanical equations for the random values of angular momenta and analyze their properties. To focus on the angular part (or the *geometry factor*) of the characteristics of the interaction of light with molecules, we limit ourselves to an approximation of the broad spectral content of the light used for excitation, which excludes the dependence on the velocities and coordinates of the particles. To become acquainted with the processes associated with the monochromatic excitation of atoms and velocity selection, one can use Ref. 24 and the references therein.

The final section is devoted to a brief survey of other methods of optical alignment and the orientation of molecules: fluorescent population, photo-dissociation, polarization in anisotropic collisions, the orientation of polar molecules in an electric field, etc.

There is great value in the information gained from experiments with polarized diatomic molecules in the ground state. Here one can separate two basic directions of research. The first is the problem of determining molecular constants, for example, the Landé factor  $g_J$  of a fixed rotational level (including a hyperfine level), the constants of hyperfine interaction and magnetic screening, and constants which characterize the interaction between terms. The importance of the problem lies in the fact that, in contrast to atoms, diamagnetic molecules have a Landé factor  $g_J$ , which, as a rule, cannot be calculated *ab initio*. On the contrary, their experi-

mental values (value and sign) make it possible to study fine processes of interaction inside the molecule (see for example, Refs. 25-30). Second, there are characteristics of the interaction with other particles: constants of velocity and the cross section of molecule-atom and molecule-molecule collisions, the orientation dependences of the parameters of chemical reactions, and even the characteristics of the interaction of molecules with a surface (absorption and reflection).

We do not claim to make a full presentation of these issues, but limit ourselves instead to examples of "test" molecules of hydrogen-like alkali dimers Na<sub>2</sub> and K<sub>2</sub>, as well as heavy molecules of iodine I<sub>2</sub> and tellurium Te<sub>2</sub>. The systems of electron transitions of these molecules in the visible part of the spectrum have been tabulated with great accuracy and are even used as wavelength standards. Laser spectroscopy methods were used to obtain information on the Frank-Condon factors, lifetimes, and other radiation and relaxation constants. For the dimers indicated, the known experience in the laser optical polarization of excited and ground states has been gathered, and a study is made of the associated phenomena of the interference of magnetic sublevels. This includes results obtained from experiments conducted in the 70s and 80s at the Latvian University.

## 2. THE DIPOLE MOMENT OF OPTICAL TRANSITIONS IN A MOLECULE

In a classical examination, the process of absorption and emission of light by a molecule can be represented by the excitation and attenuation of the oscillations of a classical Hertzian dipole  $\mathbf{d}$ . The probability of the absorption of light of course depends on the mutual orientation of this dipole and the  $\mathbf{E}$  vector of the light wave. To analyze the polarization of the molecules' angular momenta which arise in the absorption of light, one must first determine the mutual orientation of the angular momentum  $\mathbf{J}$  and the dipole moment  $\mathbf{d}$ .

The mutual orientation of the dipole moment  $\mathbf{d}$  and the internuclear axis depends on the type of molecular transition. So, for a Q $\uparrow$  type transition, where the difference in the angular momenta of the upper  $J'$  and lower  $J''$  levels  $\Delta = J' - J'' = 0$ , the dipole moment  $\mathbf{d}$  is located along the angular momentum of the molecule  $\mathbf{J}$ , and remains immobile in its rotation. In this model it is assumed that the angular momentum of the molecule does not rotate in space as a result of the absorption or emission of a photon, since the angular momentum of the photon is much smaller than the angular momentum of the molecule. In the case of P $\uparrow$  or R $\uparrow$  type transitions, where  $\Delta = J' - J'' = -1$  or  $1$ , the dipole moment of the transition rotates in the plane of rotation of the molecule. For an R $\uparrow$  type transition the direction of rotation coincides with the direction of rotation of the molecule.

For P $\uparrow$  type transitions it rotates in the opposite direction.<sup>17,31-34</sup>

The reason for this behavior of the classical dipole moment can be understood from the following. Let us first examine a molecular transition which results in an unchanged projection of the angular momentum of the electrons in the internuclear axis, for example,  $^1\Sigma \rightarrow ^1\Sigma$ ,  $^1\Pi \rightarrow ^1\Pi$ , etc. This transition is sometimes called a parallel transition,<sup>35</sup> and in this case  $\mathbf{d}$  is directed along the internuclear axis and rotates along with the molecule at a frequency  $\Omega$ . In the molecular system of coordinates, when the  $z$  axis coincides with the direction of the angular momentum of the molecule  $\mathbf{J}$ , and the  $x$  axis is directed along the internuclear axis (Fig. 3a), the unit vector of the Hertzian dipole has components

$$\mathbf{d}^{\text{mol}} = \begin{pmatrix} \exp(-i\omega_0 t) \\ 0 \\ 0 \end{pmatrix}, \quad (2.1)$$

where  $\omega_0$  is the frequency of dipole oscillations. In an immobile system of coordinates, the  $z$  axis of which, as before, coincides with the angular momentum  $\mathbf{J}$  (Figure 3b), the moment  $\mathbf{d}$  has the following components:

$$\hat{\mathbf{d}}' = \begin{pmatrix} \cos \Omega t \cdot \exp(-i\omega_0 t) \\ \sin \Omega t \cdot \exp(-i\omega_0 t) \\ 0 \end{pmatrix}, \quad (2.2)$$

where  $\Omega$  is the angular velocity of rotation of the molecule.

The polarization state of the light beam (linear, circular) is most conveniently described in polar coordinates:<sup>36</sup>

$$e_{\pm 1} = \mp \frac{1}{\sqrt{2}}(e_x \pm ie_y), \quad e_0 = e_z. \quad (2.3)$$

Actually, for example, for right-handed circular polarization of light, the polarization vector coincides with the unit vector  $e_{-1}$ . Thus, it is convenient also to write the dipole moment of the transition in this same system of coordinates, that is, in the form of Ref. 33 ( $\hat{\mathbf{d}}$  is a unit vector along  $\mathbf{d}$ )

$$\hat{\mathbf{d}}' = \begin{pmatrix} \frac{1}{2} \\ -\frac{i}{2} \\ 0 \end{pmatrix} \exp[-i(\omega_0 - \Omega)t] + \begin{pmatrix} \frac{1}{2} \\ \frac{i}{2} \\ 0 \end{pmatrix} \exp[-i(\omega_0 + \Omega)t] \\ = \hat{\mathbf{d}}_{-1} \exp[-i(\omega_0 - \Omega)t] - \hat{\mathbf{d}}_1 \exp[-i(\omega_0 + \Omega)t]. \quad (2.4)$$

To represent clearly the physical sense that we have of the real part of the first and second terms, we write the first in the form

$$\frac{1}{2} e_x \cos(\omega_0 - \Omega)t - \frac{1}{2} e_y \sin(\omega_0 - \Omega)t. \quad (2.5)$$

The resultant expression describes the rotation of a dipole

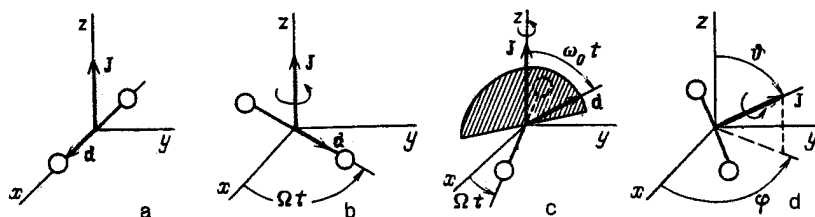


FIG. 3. Direction of the dipole moment of the optical transition in a diatomic molecule. a and b, parallel transition, P or R type; c, perpendicular transition; d, random orientation of the angular momentum  $J(\theta, \varphi)$ .

with angular velocity  $\omega_0 - \Omega$  in the plane  $xy$  in a clockwise direction; if it is seen from the end of the  $z$  axis. The second term, written in the form

$$-\frac{1}{2} e_x \cos(\omega_0 + \Omega)t - \frac{1}{2} e_y \sin(\omega_0 + \Omega)t, \quad (2.6)$$

describes rotation of the dipole in a counter-clockwise direction with an angular velocity  $\omega_0 + \Omega$ . The frequency  $\omega_0 - \Omega$  corresponds to a  $P \uparrow$  type molecular transition, which leads to a decrease in the rotation energy of the molecule. The frequency  $\omega_0 + \Omega$  corresponds to an  $R \uparrow$  type transition resulting in an increased rotation energy of the molecule. It is known that in the classical limit of a quantum examination, the rotational energy of the molecule may vary by  $\pm \hbar\Omega$ .

The situation is somewhat different for molecular transitions which result in a projection of the electron angular momentum on the internuclear axis which varies by unity. These are called perpendicular transitions,<sup>35</sup> for example,  $^1\Sigma \rightarrow ^1\Pi$ . In this case the dipole moment of the transition  $\hat{d}$  rotates with an angular velocity  $\omega_0$  in a plane which is perpendicular to the internuclear axis (Fig. 3c), and at the same time, rotates with the molecule with a velocity  $\Omega$  around the angular momentum  $J$ . In a rotating system of coordinates<sup>33</sup>

$$\hat{d}^{\text{mol}} = \begin{pmatrix} 0 \\ \exp(-i\omega_0 t) \\ i \exp(-i\omega_0 t) \end{pmatrix}. \quad (2.7)$$

Here it is also convenient, in the switch to an immobile system of coordinates, to expand the unit vector  $\hat{d}'$  into cyclic unit vectors. As a result we obtain three components. Two of them,  $\hat{d}'_{-1}$  and  $\hat{d}'_{+1}$ , as in Eq. (2.4), correspond to  $P \uparrow$  and  $R \uparrow$  type transitions at frequencies  $\omega_0 - \Omega$  and  $\omega_0 + \Omega$ . Moreover, there also arises a  $\hat{d}'_0$  component which is oriented along the  $z$  axis (that is, along the vector  $J$ ) and which makes linear oscillations with frequency  $\omega_0$ . This component corresponds to a  $Q \uparrow$  type molecular transition.

Up until now we have been interested in the orientation of the dipole moment of the transition in relation to the angular momentum  $J$  of the molecule, since it is  $J$  which maintains its orientation in space. The last assertion is true if one does not consider the effect of nuclear spin. For a nonzero nuclear spin angular momentum of the molecule there also arises in the molecule as a whole a nuclear spin  $I$ . Along with the angular momentum  $J$  it forms the total angular momentum of the molecule  $F$ . The dipole moment of the transition  $\hat{d}$ , which is linked exclusively with the electron movement of the molecules, remains, as before, coupled with the angular momentum  $J$ , and with it precesses around the total angular momentum  $F$ . The angular velocity of this precession is defined by the energy of the hyperfine interaction. For typical molecular states, where  $F \sim J \gg I$ , the hyperfine interaction has virtually no effect on the process of absorption and emission of light. Moreover, for excited molecular states the situation in Ref. 14 is typical, where the lifetime of the state is less than the period of hyperfine precession (see below Tables III and IV). This also reduces the effect of the hyperfine interaction on the process of light emission in molecules. Nonetheless, for molecular states with small quantum numbers  $J$  this effect should, in a number of cases, be considered.<sup>37</sup> Hereinafter, except for cases where it is specially stipulated, we will not consider the effect of spin  $I$ .

The examined cases exhaust all possible dipole transitions in the absorption of light by molecules in bound states. In other cases of photo-fragmentation of molecules the situation may be more complex; see for example, Ref. 38.

Thus, the three components of the unit vector of the dipole moment are written in cyclic coordinates, and they are the  $P$  component ( $\Delta = J' - J'' = -1$ ) at frequency  $\omega_0 - \Omega$ , the  $Q$  component ( $\Delta = J' - J'' = 0$ ) at frequency  $\omega_0$ , and the  $R$  component ( $\Delta = J' - J'' = 1$ ) at frequency  $\omega_0 + \Omega$ , and these three components exhaust all possible dipole optical transitions in diatomic molecules. An important consequence of this examination is the possibility of writing the total dipole moment of the transition in the form of a certain product

$$\hat{d} = V \hat{d}_\Delta, \quad (2.8)$$

where  $\hat{d}_\Delta$  characterizes the orientation of the dipole moment relative to the angular momentum of the molecule  $J$ , or the spatial orientation of the vector  $\hat{d}$ , and the isolated factor  $V$  which is a dynamic factor of the dipole moment.

### 3. DISTRIBUTION OF THE ANGULAR MOMENTA OF MOLECULES

Let us turn to an examination of the anisotropic distribution of molecular angular momenta  $J$ , created by light, which is the cause of the aforementioned anisotropy of dipole moments, which are in turn coupled with  $J$  (see Fig. 3). One should clarify how the shape of the distribution of  $J$  is connected with the angular part of the absorption probability, how it is characterized, and how the distribution is manifested in the polarization characteristics of radiation.

#### 3.1. Angular dependence of the probability of absorption

Hereinafter we will focus on the probability of light absorption by a molecule with a specific polarization. It is known that the probability of absorption of an electromagnetic wave by a Hertzian dipole is  $|\hat{E}\hat{d}|^2$ , where  $E$  is the electric vector of the light wave. This probability, proceeding from Eq. 2.8, can be divided into a dynamic  $\Gamma_p$  and an angular  $|\hat{E}\hat{d}|^2$  part. Then

$$|\hat{E}\hat{d}|^2 = \Gamma_p |\hat{E}\hat{d}_\Delta|^2. \quad (3.1)$$

The analog of this division in a quantum examination of the absorption process is the use of the Wigner-Eckhart theorem.<sup>36,39</sup> The angular part of the absorption probability is in essence no different than the law of conservation of angular momentum in the absorption of light. This is the decisive factor in the generation of the polarization of angular momenta in the excited and ground states of molecules, as well as the generation of polarization properties of radiation; thus, hereinafter we will focus on the angular part. For molecules with the vector  $J$  along the  $z$  axis the angular dependence of the absorption probability is  $|\hat{E}\hat{d}_\Delta|^2$ . In a random orientation we should project  $J$  on the  $z$  axis using Wigner's  $D$ -matrix,<sup>36</sup> which depends on the spherical angles  $\theta$  and  $\varphi$  of the orientation of  $J$  in space (Fig. 3d). Then the angular probability of light absorption  $G(\theta, \varphi)$  for a molecule with a specific orientation  $J(\theta, \varphi)$  is

$$G(\theta, \varphi) = \left| \sum_q (-1)^q \hat{E}_{-q} D_{q-\Delta}^{(1)}(\varphi, \theta, 0) \right|^2, \quad (3.2)$$

TABLE I. Explicit form of coefficients  $D_{q\Delta}^1(\varphi, \theta, 0)$ .  $\Delta$  defines the type of molecular transition,  $q$  the light polarization.

$\Delta =$	1 (R)	0 (Q)	-1 (P)
$q:$			
1 (r)	$e^{-i\varphi} \frac{1 + \cos \theta}{2}$	$-e^{-i\varphi} \frac{\sin \theta}{\sqrt{2}}$	$e^{-i\varphi} \frac{1 - \cos \theta}{2}$
0	$\frac{\sin \theta}{\sqrt{2}}$	$\cos \theta$	$-\frac{\sin \theta}{\sqrt{2}}$
-1 (l)	$e^{i\varphi} \frac{1 - \cos \theta}{2}$	$e^{i\varphi} \frac{\sin \theta}{\sqrt{2}}$	$e^{i\varphi} \frac{1 + \cos \theta}{2}$

where  $\hat{E}_Q$  are the cyclic components of the light polarization vector  $\hat{E}$ . The explicit form of the matrix  $D_{Q\Delta}^{(1)}(\varphi, \theta, 0)$  is given in Table I.<sup>36,40</sup> We can use it, for example, to obtain the angular dependence of Q $\uparrow$  absorption in the absorption of light which is linearly polarized light along the z axis

$$G(\theta, \varphi) = \cos^2 \theta. \quad (3.3)$$

As a result of the absorption of weak light (that is, without disrupting the isotropy of the distribution of angular momenta of the ground state) in the excited state there arises the distribution of angular momenta  $\rho_b(\theta, \varphi)$  shown in Fig. 4a. The shape of the distribution which is presented is completely described by the shape of the angular part of the absorption probability  $G(\theta, \varphi)$ .

### 3.2. Probability density

The function  $\rho(\theta, \varphi)$  is the probability density of the distribution of angular momenta  $\mathbf{J}$ , and means that  $\rho(\theta, \varphi) \sin \theta d\theta d\varphi$  is the probability of observing the angular momentum  $\mathbf{J}$  at spherical angles  $\theta$  to  $\theta + d\theta$ ,  $\varphi$  to  $\varphi + d\varphi$ . Knowledge of the form of the function  $\rho(\theta, \varphi)$  of the ensemble yields all the information on the polarization and coherence of the state. Normalizing the probability density

$$\int_0^\pi \int_0^{2\pi} \rho_b(\theta, \varphi) \sin \theta d\theta d\varphi = W, \quad (3.4)$$

that is, the total probability  $W$  of observing molecules in the excited state, defines the dynamic part of light absorption probability.

The distribution of angular momenta given in Fig. 4a corresponds to the alignment of the ensemble, and in this case the alignment is positive. If linearly polarized light stimulates a P $\uparrow$  or R $\uparrow$  transition, then due to the orthogonal

orientations of  $\mathbf{J}$  and  $\mathbf{d}$ , the angular dependence of absorption is equal to

$$G(\theta, \varphi) = \frac{1}{2} \sin^2 \theta. \quad (3.5)$$

If the exciting light is weak, then in the excited state there arises the distribution of angular momenta  $\rho_b(\theta, \varphi)$  shown in Fig. 4b. In this case too the ensemble is aligned, only the sign of alignment is negative.

Finally, in absorption of circularly polarized light with right-handed polarization ( $\hat{E}_{+1}$ ) which is propagating along the z axis, the angular dependence of the absorption probability in an R $\uparrow$  transition is equal to

$$G(\theta, \varphi) = \frac{1}{4} (1 - \cos \theta)^2. \quad (3.6)$$

This means that the angular part of the light absorption probability for  $\mathbf{J}$  directed opposite the light beam, that is, when the directions of rotation of  $\mathbf{d}$  and  $\mathbf{E}$  coincide, is equal to unity. If  $\mathbf{J}$  is directed along the light beam, the probability is equal to zero (Fig. 4c). In this case there is a dominant direction of orientation of angular momenta along the z axis and the ensemble of angular momenta is said to be oriented.

### 3.3. Expansion in terms of multipoles. Coherence.

The anisotropy of the distribution created by an external effect which is electromagnetic in nature has the simplest characteristics with a completely determined physical sense, if, instead of a continuous function  $\rho(\theta, \varphi)$  we use<sup>36</sup> discrete coefficients of expansion of this function in spherical harmonics

$$\rho(\theta, \varphi) = (4\pi)^{-1/2} \sum_{K=0}^{\infty} \sum_{Q=-K}^K (2K+1)^{1/2} \rho_Q^K Y_{KQ}^*(\theta, \varphi). \quad (3.7)$$

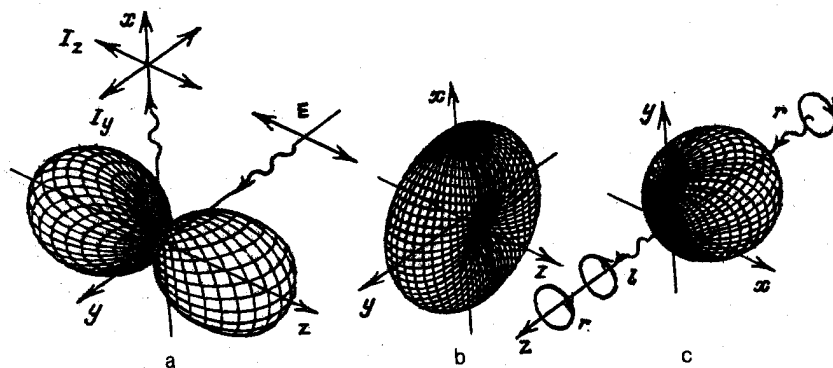


FIG. 4. Isometric projections of the probability density  $\rho_b(\theta, \varphi)$  of the distribution of the angular momentum of an excited molecular state for weak excitation. a. Q $\uparrow$  transition, linearly polarized excitation; b. P $\uparrow$  or R $\uparrow$  transition, linearly polarized excitation; c. R $\uparrow$  transition, excitation by light with right-handed circular polarization.

The selection of  $Y_{KQ}$  functions<sup>32,33</sup> as a basis was extremely successful in the sense that only a small number of expansion coefficients  $\rho_Q^K$  differed from zero. These came to be known as polarization (or multipole) moments. Thus, instead of the continuous function of two arguments, we describe the distribution with several numbers  $\rho_Q^K$ , which have the following interpretation. The moment  $\rho_0^K$  of order  $K = 0$ , in normalization according to Ref. 41, yields the probability of observing particles with a random orientation of angular momentum  $\mathbf{J}$  in an examined state. It is of course a scalar value, and it remains unchanged for any rotation of the system of coordinates. Three coordinates ( $Q = -1, 0, 1$ ) of the angular momentum of order  $K = 1$  form the polar components of the vector. They make it possible to find the average value of the components of the angular momentum  $\langle J \rangle_Q$ :

$$\langle J \rangle_Q = n_J |J| \frac{\rho_Q^1}{\rho_0^1}, \quad (3.8)$$

for the ensemble of molecules, where  $n_J$  is the number of molecules in the examined state. The value of  $\langle J \rangle_Q$  is proportional to the  $Q^{\text{th}}$  polar component  $\langle \mu \rangle_Q$  of the magnetic moment of the ensemble.

$$\langle \mu \rangle_Q = -g_J \mu_0 \langle J \rangle_Q, \quad (3.9)$$

where  $g_J$  is the Landé factor, and  $\mu_0$  is the Bohr magneton. It must be noted that components with  $Q \neq 0$ , in contrast to components with  $Q = 0$ , in the general case are complex values, thus their real and imaginary parts are physically observed. The polarization moment  $\rho_Q^K$  is called the ensemble orientation. Five components ( $Q = -2, -1, 0, 1, 2$ ) of the angular momentum of order  $K = 2$  are called the ensemble alignment. In the general case, the distribution of angular momenta is also characterized by moments of a higher order.

The classical polarization moments examined above are the asymptotic limit of quantum values, which are introduced as coefficients of the expansion of the density matrix<sup>42</sup> in terms of the irreducible tensor operators.<sup>36,43</sup> In the case of a quantum examination an important concept is the coherence of the ensemble of particles. The generation of coherence in a certain sense is associated with synchronization of the phases of basic wave functions, which describe various degenerate states of atoms or molecules.<sup>44</sup> Frequently, the states before and after the generation of coherence are various projections  $M$  of the angular momentum  $\mathbf{J}$  on the  $z$  axis (the quantization axis). Then the components of quantum polarization moments with a specific value  $Q$  characterize the coherence between states with  $\Delta M = Q$ .

In the case of classical multipole moments, the value of  $Q$  can be more easily clarified from the point of view of the symmetry properties of the ensemble of angular momenta relative to rotation around the  $z$  axis. Thus, the ensemble of angular momenta, characterized by  $\rho_Q^K$ , has the  $z$  axis as the axis of rotation symmetry of the order of  $Q$ . In the case  $Q = 0$  there is no coherence in the ensemble, and in the classical examination this ensemble has a full rotation symmetry relative to rotation around the  $z$  axis. This means that if the distribution of angular momenta has an axial symmetry, and if one chooses the quantization axis to be along the axis of

axial symmetry, one can characterize the ensemble using moments  $\rho_0^K$ .

The properties of rotational symmetry of the ensemble of angular momenta, which is characterized by a set of multipoles, is illustrated in Fig. 4. From these properties one can obtain yet another important correlation

$$\rho_Q^K = (-1)^Q (\rho_{-Q}^K)^*, \quad (3.10)$$

coupling the  $Q$  components of multipole moments of order  $K$ .

Another advantage of the expansion in Eq. (3.7) is the possibility of describing as efficiently as possible the relaxation processes. Thus, if the relaxation process is isotropic, the polarization moments of different orders relax independently, thus all components of a certain rank  $K$  relax at the same rate  $\Gamma_K$ .

One can make an experimental judgment on the distribution of angular momenta in the excited state using the angular distribution and polarization of fluorescence in the radiative transition of molecules from the studied level  $\nu'_a, J'_b$  to any other state (see the schematic of levels in Fig. 2). The intensity of fluorescence  $I$  with a certain polarization  $\hat{\mathbf{E}}'$  may be found if one knows the angular distribution  $\rho_b(\theta, \varphi)$  of the excited molecules

$$I = A \int \rho_b(\theta, \varphi) G'(\theta, \varphi) \sin \theta \, d\theta \, d\varphi, \quad (3.11)$$

where  $A$  is a normalization factor, which includes the dynamic part of the probability of molecular transition. Here  $G'(\theta, \varphi)$  describes the probability that, as a result of the dipole transition, the molecule will emit light which will have the orientation of the angular momentum  $\mathbf{J}(\theta, \varphi)$  and which will be registered by a photodetector which is only sensitive to light with polarization  $\hat{\mathbf{E}}'$ . Knowing the type of molecular transition which has occurred one can determine  $G'(\theta, \varphi)$  from Eq. (3.2).

Calculation of the fluorescence signal  $I$  is made much simpler if the functions  $\rho_b(\theta, \varphi)$  and  $G'(\theta, \varphi)$  are expanded in terms of multipoles:

$$I = A (-1)^{\Delta'} \sum_{K=0}^{\Delta} (2K+1)^{1/2} C_{1, -\Delta', \Delta'}^{K0} \sum_{Q=-K}^K (-1)^Q \rho_Q^K \Phi_Q^K(\hat{\mathbf{E}}'), \quad (3.12)$$

where  $\Delta = J' - J''$  is the difference in the angular momenta of the initial and final states of the fluorescence transition.  $C_{1, -\Delta', \Delta'}^{K0}$  is the Clebsch-Gordan coefficient. The value  $\Phi_Q^K$  introduced by Dyakonov<sup>45</sup> characterizes the function  $G'(\theta, \varphi)$  and is equal to

$$\Phi_Q^K(\hat{\mathbf{E}}') = \frac{1}{(2K+1)^{1/2}} \sum_{q,q'} (-1)^q \hat{E}_q \hat{E}_{q'}^* C_{1q1, -q'}^{KQ}, \quad (3.13)$$

here  $\hat{E}_q$  and  $\hat{E}_{q'}^*$  are the cyclical components of the vector  $\hat{\mathbf{E}}$ . Equations (3.12) and (3.13) demonstrate that only polarization moments of order  $K \leq 2$  directly contribute to fluorescence due to the symmetry properties of the angular probability of radiation  $G'(\theta, \varphi)$ .

This examination has shown how one can unambiguously determine the angular distribution  $\rho_b(\theta, \varphi)$  of an excited state for the case of the effect of weak light using a small number of discrete multipole moments  $\rho_Q^K$  for which  $K \leq 2$ . For example, for linear polarization of light with an optimal

TABLE II. Values of degree of polarization  $P$ , alignment  $R$ , and circularity  $C$  for various types of molecular transitions.

Transition	$\cos^2\langle\xi\rangle$	$P$	$P_{\max}$	$R$	$R_{\max}$	$C$	$C_{\max}$
$Q \uparrow Q \downarrow$	1	$\frac{3\rho_0^2}{2\rho_0^0 + \rho_0^2}$ $= \frac{3}{5(\Gamma_2/\Gamma_0) + 1}$	$\frac{1}{2}$	$\frac{\rho_0^2}{\rho_0^0} = \frac{2}{5} \frac{\Gamma_0}{\Gamma_2}$	$\frac{2}{5}$	0	0
$P \uparrow P \downarrow$	$\frac{1}{2}$	$\frac{3\rho_0^2}{\rho_0^2 - 4\rho_0^0}$ $= \frac{3}{20(\Gamma_2/\Gamma_0) + 1}$	$\frac{1}{7}$	$-\frac{1}{2} \frac{\rho_0^2}{\rho_0^0} = -\frac{1}{10} \frac{\Gamma_0}{\Gamma_2}$	$\frac{1}{10}$	$\frac{-3\rho_0^1}{2\rho_0^0 + \rho_0^2}$ $= \frac{-15\Gamma_0/\Gamma_1}{20 + (\Gamma_0/\Gamma_2)}$	$\frac{5}{7}$
$R \uparrow R \downarrow$						$\frac{3\rho_0^1}{2\rho_0^0 + \rho_0^2}$ $= \frac{15\Gamma_0/\Gamma_1}{20 + (\Gamma_0/\Gamma_2)}$	$\frac{5}{7}$
$P \uparrow R \downarrow$						$\frac{3\rho_0^1}{2\rho_0^0 + \rho_0^2}$ $= \frac{-15\Gamma_0/\Gamma_1}{20 + (\Gamma_0/\Gamma_2)}$	$-\frac{5}{7}$
$R \uparrow P \downarrow$						$\frac{-3\rho_0^1}{2\rho_0^0 + \rho_0^2}$ $= \frac{-15\Gamma_0/\Gamma_1}{20 + (\Gamma_0/\Gamma_2)}$	$-\frac{5}{7}$
$Q \uparrow P \downarrow$	0	$\frac{3\rho_0^2}{\rho_0^2 - 4\rho_0^0}$ $= \frac{-3}{10(\Gamma_2/\Gamma_0) - 1}$	$\frac{1}{3}$	$-\frac{1}{2} \frac{\rho_0^2}{\rho_0^0} = -\frac{1}{5} \frac{\Gamma_0}{\Gamma_2}$	$-\frac{1}{5}$	0	0
$Q \uparrow R \downarrow$							
$P \uparrow Q \downarrow$							
$R \uparrow Q \downarrow$							

set of coordinates there are only two:  ${}_b\rho_0^2$  (alignment) and  ${}_b\rho_0^0$  (population density).

Let us discuss how one can use a measurement of the angular distribution of radiation or its polarization to determine the value of  ${}_b\rho_0^2$ . The second method is technically more convenient; most frequently the traditional measurements of the degree of polarization (circularity), imply, as a rule, a specific geometry of excitation and observation (see Fig. 4). A summary of the expressions for the most common cases is given in Table II. We note that the degree of linear light polarization

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3 \cos^2 \langle \xi \rangle - 1}{\cos^2 \langle \xi \rangle + 3}, \quad (3.14)$$

where  $I_{\parallel, \perp}$  are the components of radiation polarized either parallel or orthogonal to the vector  $\mathbf{E}$  of the light used for excitation (see Fig. 4a). Here  $\xi$  is the angle between the absorbing and radiating dipole,<sup>14</sup> and averaging is done for the molecular ensemble over the lifetime of the excited state, which usually greatly exceeds the period of rotation of the molecule. The values of  $\cos^2 \langle \xi \rangle$  are given in Table II.

It is clear from Table II that Eq. 3.14 is not completely suitable, since  ${}_b\rho_0^2$  is also in the denominator. Thus, frequently Refs. 39 and 46 use the "degree of alignment."

$$R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{2}{5} (3 \cos^2 \langle \xi \rangle - 1), \quad (3.15)$$

which is suitable because it is the ratio of alignment to population density  ${}_b\rho_0^2/{}_b\rho_0^0$  (see Table II). The degree of circularity in the geometry of Fig. 4c is

$$C = \frac{I_s - I_o}{I_s + I_o}, \quad (3.16)$$

where  $I_s$  and  $I_o$  are the intensity of fluorescence circularly polarized in the same or the opposite direction as the light used for excitation. The maximum values determined from Eqs. (3.14)–(3.16) (see Table II) are taken in the case where all the polarization moments relax at the same rate  $\Gamma_{\kappa} = \Gamma$ ; that is, there are no depolarizing collisions. If this is not so, measurements of  $P$  or  $R$  can be used to determine the ratio of constants  $\Gamma_2/\Gamma_0$ , as well as of the effective cross sections  $\sigma_2/\sigma_0$  of the relaxation of alignment, and population density. We note that there is a "magic" angle  $\theta_0$  for the position of the analyzer axis with respect to the vector  $\mathbf{E}$ , which is equal to  $\theta_0 = \arccos(1/\sqrt{3})$ , at which the recorded intensity  $I_{\theta_0}$  does not contain  ${}_b\rho_0^2$ , and thus is linked only to  $\Gamma_0$ . One can not determine  $\Gamma_1/\Gamma_0$  directly from the degree of circularity for orientation because alignment also arises.

Bain and McCaffrey<sup>47</sup> examined the question of setting up the experiment in the geometry of making observations along the beam. This arrangement makes it possible to determine all three components  $\Gamma_0$ ,  $\Gamma_1$ , and  $\Gamma_2$  by making a series of measurements as the analyzer is rotated through different angles. It is shown in Ref. 48 that the ability to determine  $\Gamma_1$  yields the Hanle effect with the use of elliptically polarized light.

Experiments in which the cross sections  $\sigma_0$  and  $\sigma_2$  are determined separately for diatomic molecules are not as numerous as those for atoms. For example, in Ref. 49 it was found that  $\sigma_2/\sigma_0 \approx 1.6$  for the hydride  $\text{CdH}(A^2\Pi_{1/2}) + \text{Ar}$ ,  $\nu' = 0, J' = 16.5$ . The very small differences between  $\sigma_2$  and  $\sigma_0$  were found at high pressures, 100–600 Torr, in the work of Kolwas and Szönert<sup>50</sup> for  $\text{Na}_2(B^1\Pi_u) + \text{He}$ ; thus for  $\nu' = 10, J' = 10, \sigma_2 - \sigma_0 = (1.4 \pm 0.5) \cdot 10^{-16} \text{ cm}^2$ . Similar values were obtained by the authors of Ref. 51 for  $\text{Li}_2$ . In Ref. 52, the method of double resonance was used for collisions of  $\text{CO} + \text{CO}$ , and it was found that  $\sigma_2/\sigma_0 \approx 1.5$  for  $J = 9$ . In Refs. 53–55 no laser-induced fluorescence depolarization was found for  $\text{Te}_2(\text{AO}_u^+)$ ,  $\text{K}_2(B^1\Pi_u)$  and  $\text{NaK}(D^1\Pi)$  at inert gas pressures of up to several Torr. This indicates the low efficiency of depolarizing collisions. These data appear to confirm the fact that, at least for dimers, it is easier to “extinguish” than to depolarize the fluorescence of diatomic molecules, an opinion which has been held for a long time.<sup>17</sup> There is a great number of papers, for example, Refs. 51, 56–60, which study the transmission of orientation to other rotation levels in collisions of  $\text{I}_2$ ,  $\text{Li}_2$ , and  $\text{NaK}$  with an inert gas.

Here one should bear in mind the different sense of purely depolarizing collisions, which are expressed in the form of a difference of cross sections,  $\sigma_2 - \sigma_0$  or  $\sigma_1 - \sigma_0$ , which are effective in the rotation of  $J$  on average by  $\pi/2$  and  $\pi$  respectively without a change in the other quantum numbers  $\nu'$  and  $J'$ . However, rotation of  $J$  by such a large angle (collisional randomizing) when  $J' \gg 1, \Delta E_J \ll kT$ , as noted in Ref. 12, leads with great probability to a change in the value of  $J'$  itself, that is, to a transition to another rotational level.

#### 4. MANIFESTATION OF ANISOTROPY OF THE GROUND STATE

Up until now the examination has been limited to the excited state of simple molecules. Of fundamental impor-

tance is the extension to molecular objects of Kastler methods of creating a nonequilibrium situation in the magnetic sublevels of the ground state. Let us turn to an examination of the specifics of radiation and relaxation processes caused mainly by the vibrational and rotational structure of the electron transition in the molecule (see Fig. 2).

##### 4.1. Description of the method

We shall, as earlier, assume a broad-band excitation where the spectral width exceeds the homogeneous and inhomogeneous contour associated with the transition. In this case the internal variables are separated from the external variable, the velocity of the translational motion of the particle. Such a situation may occur, to some degree, for example, in the excitation by lines of gas lasers of many axial asynchronous modes in the generation regime. Wide excitation lines are approximated<sup>61,62</sup> if the distance between the modes is less than the width of the Bennett gap, and a large number of axial modes fall within the Doppler contour. For narrow excitation lines the situation is more complex; see Refs. 4, 24, 63–66, and the references therein. For wide excitation line conditions, the dynamic part of the absorption probability which does not depend on angles, Eq. (3.1), may be characterized by the rate  $\Gamma_p$  of the depopulation of level  $\vartheta_a'', J_a''$ . The spontaneous decay of the upper level  $b$  occurs at a rate  $\Gamma$ . The probability of transitions to various  $\nu_i''$  determines<sup>67–69</sup> the Frank-Condon factors, the electron forces of the transition, and the frequency factor  $\nu^3$ . A return to the initial level, which is characterized by the rate  $\Gamma_{ba}$  is rather unlikely, usually  $\Gamma_{ba}/\Gamma \ll 1$ .

For orientation in more or less characteristic values of the dynamic parameters in saturated vapors, the data in Table III can be used. These data are for the dimers  $\text{K}_2$  and  $\text{Te}_2$ . These objects were chosen as being the most studied in optical pumping regime. The sources of excitation were standard lines of the most common mass-produced He-Ne and  $\text{Ar}^+$  lasers. This guarantees reliable assignment of the vibrational and rotational numbers of the transitions. Now tunable lasers are widely used, which make it possible to “sort” the set of vibration-rotation states; see examples in Ref. 77.

The next radiation channel is induced transitions. Their contribution is estimated from the ratio  $\Gamma_p/\Gamma$ , which is in our example, as is clear from Table III, less than 0.004 for  $\text{K}_2$  and about 0.1 for  $\text{Te}_2$ .

Thus, the main process which competes with light ab-

TABLE III. Basic characteristics of electron vibration-rotation levels and transitions of  $\text{K}_2$  and  $\text{Te}_2$  in laser fluorescence experiments with optical polarization of the ground state. Numbers in square brackets are references.

Parameters	<sup>39</sup> K <sub>2</sub>	<sup>130</sup> Te <sub>2</sub>
$\lambda_{\text{exc}}, \text{ nm}$	632.8	514.5
$a$ , or $(\alpha', \nu', J')$	(X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> , 1.73)	(XO <sub>g</sub> <sup>+</sup> , 6.52)
$b$ , or $(\alpha', \nu', J')$	(B <sup>1</sup> Π <sub>u</sub> , 8.73)	(AO <sub>u</sub> <sup>+</sup> , 11.53)
$T, \text{ K}$	441	630
$N, \text{ cm}^{-3}$	[K] = $0.3 \cdot 10^{14}$ [70]	[Te <sub>2</sub> ] = $0.8 \cdot 10^{14}$ [74]
$\gamma, 10^6 \text{ s}^{-1}$	0.13–0.23 [71,76,90]	0.39–0.41 [125,138]
$\sigma, 10^{-14} \text{ cm}^2$	3.3 for (K <sub>2</sub> + K) [76]	4 for (Te <sub>2</sub> + Te <sub>2</sub> ) [125]
$\Gamma, 10^6 \text{ s}^{-1}$	86.2 [71]	1.49 [53]
$\Gamma_p, 10^6 \text{ s}^{-1}$	0.22–0.35 [71,76,90]	0.12–0.16 [125, 138]
$\Gamma_{J,J'}, 10^6 \text{ s}^{-1}$	3.78 [72]	0.037 [75]
$g_J, 10^{-4}$	$1/J' (J' + 1) = -1.85$ [14]	0.52 [53]



sorption is relaxation in the system of vibrational and rotational levels of the lower state  $\alpha''$ , which includes: a) transitions induced by collisions b) relaxation due to the finite time in which the molecule is in the zone of interaction with the optical field (time of flight); c) spontaneous radiative transitions within one electron term. The last mechanism is excluded for homonuclear diatomic molecules (dimers). Collision relaxation is determined in various experiments through the effective cross section  $\sigma$  and the concentration of particles  $N$ , and in a volume of rarified gases may be of the order  $\gamma_{\text{col}} = N\sigma v_{\text{rel}} \approx 10^4 - 10^7 \text{ s}^{-1}$ ; see examples in Table III;  $v_{\text{rel}}$  is relative velocity.

The second mechanism is associated with the exchange between polarized particles inside the beam and unpolarized particles from the remaining volume. Usually, the zone of action of laser radiation is much smaller than the volume filled with gas particles. Thus, the ground state, even in the absence of collisions, has an effective "lifetime"  $T_0$  of the order of the average transit time through the beam. In beam experiments,  $T_0^{-1}$  is, as a rule, the dominant rate of relaxation. The process of optical polarization will be effective only when  $\Gamma_p T_0 > 1$ . Although the order of magnitude of  $T_0$  can be easily determined from the effective diameter of the laser beam divided by the average velocity in the plane perpendicular to the beam, one must consider the fact that the transit time for each particle depends on its trajectory and the velocity of movement through the beam with a given profile of power density distribution in the cross section of the laser pump beam; thus, the kinetics of relaxation in the general case are nonexponential. Calculations and experiments on the ground state of molecules can be found in Refs. 73 and 78; for atoms, see Ref. 79.

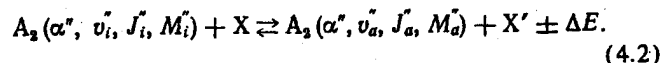
It is important to note that if for an excited state one can correctly introduce the effective relaxation rate  $\Gamma = \tau_{sp}^{-1} + \Gamma_{\text{col}}$ , where  $\Gamma_{\text{col}}$  is the rate of collision relaxation, then for the ground state, as follows from Refs. 73, 78, and 79, a similar additive introduction of the total rate

$$\gamma_{\Sigma} = T_0^{-1} + \gamma_{\text{col}} = T_0^{-1} + N\sigma v_{\text{rel}} \quad (4.1)$$

is not always possible due to the nonexponential character of the transit time relaxation. Strictly speaking, this "collision" consideration of the transit time using the constant  $T_0$  is correct only for the case of a laser beam which is homogeneous over a circular cross section, or in the case where collisions dominate,  $\gamma_{\text{col}} \gg T_0^{-1}$ . Specially created "transit" conditions with a known  $T_0$  can be used to normalize the relative measurements in the time scale, and more will be said about this below.

Let us return now to the collision mechanism of relaxation of level  $a$  (see Fig. 2). Let collisions  $A_2 - X$  attempt to

restore the occupancy of the lower level  $a$  to thermal equilibrium by mixing with another level  $i$  in the reaction



In the majority of cases the process of rotational mixing will dominate. Direct beam experiments make it possible to form an opinion about this.  $\text{Na}/\text{Na}_2$  is an inert gas with fixed initial and final states in the investigations of Bergman *et al.*<sup>80-82</sup> and Serri *et al.*<sup>83</sup> Since the number of levels  $i$  is usually large (transitions with  $|J_i'' - J_a''|$  up to 20 and even up to 80 have been observed) and in common cases  $\Delta E_{ia} = E_i - E_a \ll kT$ , they are commonly modeled by a thermostat of isotropic states that are not affected by the cycle of optical pumping. A definite confirmation of this model is the experiment with  $\text{Li}_2(X^1\Sigma_g^+)$  (Ref. 84).

Thus, one can conclude that the resulting steady-state polarization (alignment, orientation) of some lower level which is an initial level in optical absorption will be determined by a competition of rates of absorption  $\Gamma_p$  and relaxation  $\gamma_{\Sigma}$ . If their ratio, which is in essence a dimensionless pumping parameter,  $\chi = \Gamma_p/\gamma_{\Sigma}$ , is comparable with unity, the distribution of angular momenta of the ground state  $J_a(\theta, \varphi)$  will cease to be isotropic; that is, the probability density which characterizes it,  $\rho_a(\theta, \varphi)$ , will no longer be spherically symmetrical (Figs. 5b and 5d). Let us now turn to a description of the manifestation of this effect in fluorescence.

#### 4.2. Nonlinear effects in the intensity and polarization of radiation

Let us apply the classical approach which has been presented above to the case where  $\Gamma_p \gtrsim \gamma_{\Sigma}$ , that is, where there is optical polarization of level  $a$  (see Figs. 2 and 5).

Let us examine a very simple balance equation for the probability density of angular momenta of an absorbing state

$$\begin{aligned} \dot{\rho}_a(\theta, \varphi) &= -\Gamma_p G(\theta, \varphi) \rho_a(\theta, \varphi) + \gamma_{\Sigma} [\rho_a^0 - \rho_a(\theta, \varphi)], \\ \dot{\rho}_b(\theta, \varphi) &= \frac{\Gamma_p}{\Gamma} G(\theta, \varphi) \rho_a(\theta, \varphi), \end{aligned} \quad (4.3)$$

where  $\rho_a^0$  is the isotropic population density. Then for the steady-state case

$$\rho_a(\theta, \varphi) = \rho_a^0 (1 + \chi G(\theta, \varphi))^{-1}. \quad (4.4)$$

Using the angular coefficients of absorption  $G(\theta, \varphi)$  from Eqs. (3.3) and (3.5) one can clearly represent the distribution of angular momenta of the lower state  $J_a(\theta, \varphi)$  (see Figs. 5b and 5d).

Let us examine the  $Q\uparrow$  absorption directed along the  $z$

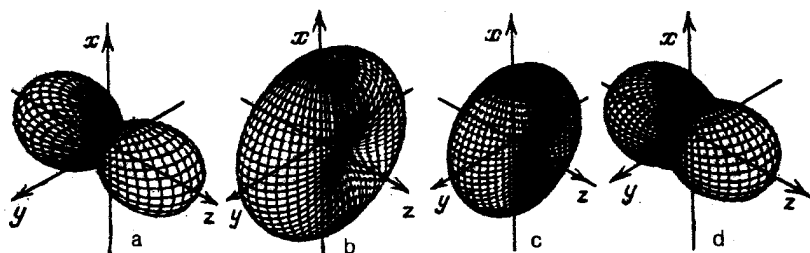


FIG. 5. Isometric projections of the probability density of the distribution of angular momenta of the ground (a and b) and excited (c and d) states. a. and b.  $Q\uparrow$  excitation, c. and d.  $P\uparrow$ ,  $R\uparrow$  excitation.

axis of linearly polarized light in the geometry of Fig. 4. In this case a volume in the form of a dumbbell is "eaten out of" the spherical distribution of angular momenta of the ground state. This dumbbell is transferred to the excited level  $b$  (see Fig. 5a). The scale of  $\rho_b$  in the figure was chosen with a consideration of the factor  $\Gamma/\gamma_z$  so that the sum of  $\rho_a$  and  $\rho_b$  again forms a sphere. It is clear that in the lower state a negative alignment is created along the  $z$  axis. This is clear from the dipole model (see section 2), since for the  $Q\uparrow$  transition,  $d\parallel J$  and the classical dipole moments of the transition do not rotate.

For  $P\uparrow, R\uparrow$  transitions the angular momenta of the lower state  $J_a$  have positive alignment along the  $z$  axis or along the vector  $E$  (see Fig. 5d), which directly follows from the orthogonal nature of  $d\perp E$ . Here  $\rho_a$  and  $\rho_b$  add up to a sphere in Figs. 5c and 5d.

Let us now turn to expressions for the observed signals. The simplest is the effect observed in the intensity and polarization of fluorescence, which is excited by the pumping beam, for example, in some convenient transition  $b \rightarrow c$  (see Fig. 2). In the approximation of the balance equations (4.3) and (4.4) analytical expressions for the intensity and degree of polarization in a  $Q\uparrow Q\downarrow$  transition have been given in Ref. 11 for the geometry in Fig. 4. They were obtained by substituting  $\rho_b(\theta, \varphi)$  from Eqs. (4.3) into Eqs. (3.11) and (3.14), bearing in mind the rules indicated for finding the angular coefficients  $G(\theta, \varphi)$  and  $G'(\theta, \varphi)$ , and have the simple form

$$\begin{aligned} QI_{\parallel} &= \Gamma_p \rho_a^0 \chi^{-1} \left( a\chi^{-3/2} - \chi^{-1} + \frac{1}{3} \right), \\ QI_{\perp} &= \Gamma_p \rho_a^0 \chi^{-1} \left( -a\chi^{-3/2} - a\chi^{-1/2} + \chi^{-1} + \frac{2}{3} \right), \\ QP &= \frac{3a\chi^{-1/2} (3\chi^{-1} + 1) - 9\chi^{-1}}{3a\chi^{-1/2} (\chi^{-1} - 1) - 3\chi^{-1} + 4}, \\ a &= \text{arctg } \chi^{1/2}. \end{aligned} \quad (4.5)$$

It is clear that the dimensionless value, the degree of polarization  $QP$ , depends only on one parameter which is also dimensionless,  $\chi$ . Thus, the dependence  $QP(\chi)$  (Fig. 6b) is like a calibration curve, which makes it possible to determine immediately the value  $\chi = \Gamma_p/\gamma_z$ . The value of  $QP$  decreases as  $\chi$  increases because the intensity  $QI_{\parallel}$  is more saturated than  $QI_{\perp}$  (Fig. 6a). The reason for "depolarization" due to the alignment of the lower state may be understood from the shape of the distribution  $J_a(\theta, \varphi)$  (Fig. 5b). Actually, the deficit in the number of particles with  $J_a \parallel E$  ("negative" alignment) generates a deficit of particles with  $J_b \parallel E$  in the excited state, and it is these molecules which make the predominant contribution to  $QI_{\parallel}$ . As a result the distribution in Fig. 5a is less "extended" along the  $z$  axis than in weak excitation (Fig. 4a).

The first experiment<sup>11</sup> showed a noticeable decrease in  $QP$  in the transition  $(X^1\Sigma_g^+, 3.43) \rightarrow (B^1\Pi_u, 6.43) \rightarrow (X^1\Sigma_g^+, 13.43)$  in  $\text{Na}_2$  with an increase in the power density of the radiation of the Ar laser (488.0 nm) used for excitation. Figure 6a gives curves<sup>85</sup> for  $QI_{\parallel, \perp}$  for the same transition, while Fig. 6b gives the corresponding dependence  $QP(\chi)$  obtained from Eq. (4.5).

The expressions for a  $P, R$  type transition in excitation and radiation have the form

$$\begin{aligned} P, R I_{\parallel} &= \Gamma_p \rho_a^0 (b^2 - 1) \left[ c(b^3 - 2b + b^{-1}) - b^2 + \frac{5}{3} \right], \\ P, R I_{\perp} &= \frac{\Gamma_p \rho_a^0}{2} (b^2 - 1) \left[ c(b^{-1} - b^3) + b^2 + \frac{1}{3} \right], \\ P, R P &= \frac{c(3b^3 - 4b + b^{-1}) - 3b^2 + 3}{c(b^3 - 4b + 3b^{-1}) - b^2 + (11/3)}, \\ b^2 &= 1 + 2\chi^{-1}, \quad c = \text{Arth } b^{-1}. \end{aligned} \quad (4.6)$$

The cause of "depolarization" as  $\chi$  increases for  $P, R$  type transitions which was first recorded<sup>86</sup> in  $I_2$ , can be understood in the classical model from the following considerations. The oscillators  $d\perp J$  rotate around  $J$  (see Fig. 3) so in conditions of positive alignment  $J_a(\theta, \varphi)$  in Fig. 5d, there are fewer  $d$  which rotate in the  $xz$  and  $yz$  planes. Predominant are  $d$  which rotate in the  $xy$  plane, that is, perpendicular to  $E\parallel Oz$ . It is these oscillators that, after absorption, make a larger contribution to the intensity  $P, R I_{\perp}$ , which is polarized in the same  $xy$  plane, than to the orthogonally polarized intensity  $P, R I_{\parallel}$ . This leads to a decrease in the degree of polarization compared with the case of a spherical distribution of  $J_a$ . Later,<sup>87</sup> the optical orientation of the ground state of  $\text{Na}_2(X^1\Sigma_g^+, 2.45)$  was recorded in the excitation of the  $X \rightarrow A$  transition by circularly polarized light. The expressions for the dependence  $P(\chi)$  for states with finite  $J$  can be found in Ref. 88.

The first application of the effects was the determination of the rates and cross sections of relaxation processes of the polarization produced in the lower state. Drullinger and Zare<sup>12</sup> determined from  $QP$  the dependence of  $\chi = \Gamma_p/\gamma_z$  on the pressure of the admixed inert gases and also of  $\text{H}_2, \text{N}_2,$  and  $\text{CH}_4$ . For a transition with relaxation rate  $\gamma_z$ , the kinetics were measured of establishing optical alignment after the pump was switched on.<sup>12</sup> Similar measurements were made in Ref. 89 for the molecule  $I_2(X^1\Sigma_g^+, 0.13$  and  $15)$ . To determine the effective cross sections, the authors of Refs. 12 and 89 obtained a nonlinear dependence  $\chi^{-1} \sim \gamma_z$  from the concentration  $N$  with a break at small  $N < N'$ . The values of the cross sections at  $N > N'$ , which were determined from Eq. (4.1), were about  $10^{-14} \text{ cm}^2$ . They basically reflect collision relaxation due to the rotation transitions  $J'' \rightarrow J''_a$ . Similar cross section values were obtained using the same

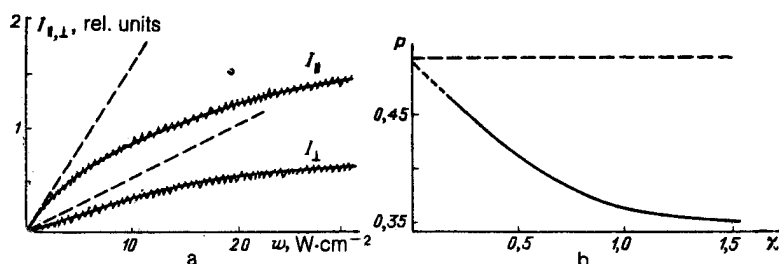


FIG. 6. a and b. Manifestation of nonlinear optical alignment in intensity  $I_{\parallel}, I_{\perp}$  (a) and the degree of linear polarization  $P$  (b) of fluorescence.  $w$  is the power density of the laser used for excitation,  $\chi = \Gamma_p/\gamma_z$  is the pumping parameter. The dashed line is the linear limit of weak excitation,  $\chi = 0$  (Ref. 85).

method<sup>90,91</sup> for  $K_2$  and  $Na_2$ . At the same time, the interpretation of the behavior of  $\chi(N)$  at  $N < N'$  as elastic collisions which fill the Bennett gap is unlikely to be true. This interpretation has not been confirmed in direct measurements of the relaxation kinetics.<sup>73,76,92,93</sup> It is more likely that due to the decisive role of the passage through the beam at small  $N$  one cannot use Eq. (4.1). The break is artificial, as was shown in Refs. 73 and 78. Equation (4.1) can be used if a homogeneous distribution of laser power is formed over a circular cross section of the beam of radius  $r_0$ ; then<sup>78</sup>

$$T_0^{-1} \approx 0,854 \langle v_{\text{prob}} \rangle r_0^{-2}, \quad (4.7)$$

where  $\langle v_{\text{prob}} \rangle$  is the most probable velocity of the molecules.

The use of this condition in Eq. (4.1) makes it possible to switch to a temporal scale by extrapolation of  $P(\chi)$  to  $N \rightarrow 0$ . This was used<sup>94,95</sup> to solve, in some sense a reverse problem, -determination of  $\Gamma_p$  to measure the absolute concentration of  $K_2$  molecules in potassium vapor. The data obtained in the temperature range 470–525 K agrees well with data from Ref. 70.

To study in detail the relaxation processes in the ground state of dimers, a "two-laser" method was used, with a probe beam at a different wavelength. Thus, Ottinger and Schröder<sup>84</sup> used the intense radiation of an  $Ar^+$  laser to depopulate optically  $Li_2(X^1\Sigma_g^+, 1.24)$  while recording the fluorescence excited by a dye laser from neighboring levels  $J''_a + \Delta J''$ ,  $\Delta J'' = (2, 4, \dots, 14)$ . They determined the cross sections of transfer processes in collisions with He, Ne, Ar, Kr and Xe, which were equal to  $5 \cdot 10^{-16}$  to  $8 \cdot 10^{-16}$   $cm^2$  for  $\Delta J'' = 2$ . Here optical depopulation was used as a "marker" of the lower vibration-rotation level. The approach is of a very general nature, since it is the basis of methods using signals with a modulated level occupancy; see the survey in Ref. 96, and the survey of laser polarization spectroscopy,<sup>97,98</sup> which will be discussed in more detail in the following section.

### 4.3. Transition process

The possibility of directly determining the rate of relaxation is provided by the kinetics of the transition process following an "instantaneous" switching on or off of the pumping beam. The first experiment of this type involving the ground state of molecules was carried out by Schawlow's group.<sup>92</sup> The authors measured the kinetics of "repopulation" (restoration of the occupancy) of a state of  $Na_2(X^1\Sigma_g^+, 0.47)$  depopulated by an intense pulse from a dye laser in the process of the  $X \rightarrow B$  transition based on the time dependence of the coefficient of absorption of a weak probe dye laser which initiated the  $X \rightarrow A$  transition from the same level  $v''_a, J''_a$ . The laser fluorescence method turned out to be more sensitive. This method was proposed simultaneously in Refs. 76 and 93. In the simplest variation (Fig. 7), an intense laser beam is periodically "instantaneously" attenuated, becoming a probe laser. The time dependence of fluorescence in this type of modulation is recorded in an  $a \rightarrow b \rightarrow c$  scheme (see Fig. 2) given in Fig. 7b. Region 1 corresponds to the establishment of pumping to a steady state (region 2). The most convenient region for determining  $\gamma_x$  is region 3, since the increase in intensity at  $t > t_0$  directly reflects the thermalization of the depopulated level to an equilibrium (region 4). The process in region 3 is linear in

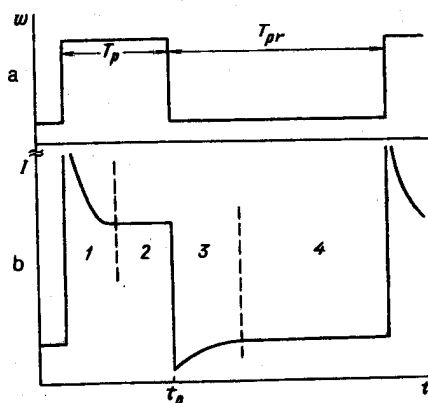


FIG. 7. a and b. Using the transition process method, the dependence on time for excitation radiation (a) and for the intensity of fluorescence (b).

absorption, and in the case of a predominance of collisions over transit, can be considered to be monoexponential. Here it is necessary to have  $T_p^{-1}, T_{pr}^{-1} \gg \gamma_r + \Gamma_p$ . The effective cross sections for relaxation of  $K_2(X^1\Sigma_g^+, 1.73)$  with all inert gases<sup>73</sup> is from  $0.5 \cdot 10^{-14}$  to  $1.6 \cdot 10^{-14}$   $cm^2$ . Similar results were obtained in Ref. 93 for  $Na_2$ .

Reference 101 examines the question of how the polarization moments of the ground state  $\rho_0^x$ , which relax in isotropic collisions with rates  $\gamma_x$ , are manifested in a linear transition process (region 3). If it is assumed that  $\Gamma_x \gg \gamma_x$ , then the radiation kinetics at  $t > t_0$  (Fig. 7b) is "controlled" on the  $\gamma_x^{-1}$  scale by the time dependence of  ${}_3\rho_0^x(t)$ :

$$\begin{aligned} {}_3\rho_0^x(t) &= -({}_4\rho_0^x - {}_2\rho_0^x) \exp[-\gamma_0(t - t_0)] + {}_4\rho_0^x, \quad x = 0, \\ {}_3\rho_0^x(t) &= {}_2\rho_0^x \exp[-\gamma_x(t - t_0)], \quad x \neq 0, \end{aligned} \quad (4.8)$$

where  ${}_2\rho_0^x, {}_4\rho_0^x$  correspond to regions 2 and 4 in Fig. 7b. Here it is interesting that, for example, in the case of an extremely weak linearly polarized excitation, moments are manifested of the order  $x = 0, 2, 4$ ; that is, in the general case there can be three exponents. However, in many cases, by analogy with the data for excited states (section 3), one should not expect noticeable differences between  $\gamma_0, \gamma_2$ , and  $\gamma_4$ , which, as a rule, justifies the monoexponential approximation.

The situation is much different in the case of the predominance of transit relaxation in a Gaussian profile of the pumping beam, when Eq. (4.1) is not satisfied. Calculation and experiment<sup>73,78</sup> yield a process which is noticeably different from an exponential process in region 3 with "tightening up" in the initial part of the curve.

### 4.4. Molecular beams and magnetic resonance

Fundamentally new results are obtained in the transition from molecules in bulk to molecules in beams. First, the efficiency of depopulation of the lower level is substantially increased, since relaxation is determined only by the time of flight effect. The clearest example of this is the work of Bergman *et al.*<sup>82</sup> in which such a high degree of alignment was obtained with the use of a P, R type transition of  $Na_2$  in supersonic beams that one could speak of the "preparation" of molecules in one specific  $|M_J^x\rangle$  state. Second, in the study of collisions, the combination of optical depopulation of the  $v''_a, J''_a$  level, and the crossed beams method makes it possible

to obtain the most detailed characteristics of the elemental act of the collision transition  $v''_a, J''_a \leftrightarrow v''_i, J''_i$  in the form of differential cross sections with fixed initial and final vibration-rotation numbers. This problem has also been solved in the comprehensive series of works by Bergman *et al.* and Serri *et al.* which have already been mentioned, of which we shall refer to Refs. 80–83 (see also Ref. 77), where the differential cross sections were measured for crossed beams of Na/Na<sub>2</sub> and an inert gas. Rainbow effects were observed and the interaction potentials were determined. Measurement of the differential cross sections of inelastic rotational scattering using optical pumping techniques<sup>82</sup> made it possible to confirm the tendency for the preservation of orientation of the angular momentum (satisfaction of the rule  $|\Delta M''| \ll J''$ ). The results obtained for Na<sub>2</sub> ( $X^1\Sigma_g^+$ ) + Ne do not contradict the selection rule  $\Delta M'' = 0$ .

The application of laser optical pumping to a beam of molecules made it possible for Rosner, Holt, and Gaily<sup>99</sup> to develop the double laser radio frequency resonance technique to study hyperfine structure. The essence of the method is the combination of the magnetic resonance method in molecular beams (Rabi, Ramsay *et al.*, see Ref. 27) and the laser-fluorescence method in conditions of optical pumping. The advantages are clear: the ability to study an individual level  $v''_a, J''_a$ , no need to create powerful inhomogeneous magnetic fields, and an increase in sensitivity. The method is as follows. A beam of molecules is intersected by a laser pump beam, producing in the depopulation process a difference in the populations of the hyperfine sublevels  $F''$ . The beam of molecules then passes through an alternating magnetic field with an amplitude of about 3.5 Gauss, causing a change in the populations, which is detected "downstream" by the fluorescence caused by the other beam of the same laser. The shape of the resonance line is averaged over the factor  $\exp(-\omega_{F''} T_0)$ , where  $\omega_{F''}$  is the interval of hyperfine structure, and  $T_0$  is the time of flight of the molecule through the region of action of the radio frequency field;  $T_0$  is about 3 ms. Since the effect should be averaged over the distribution of velocities in the beam, the exponential factor under these conditions disappears at  $\omega_{F''}/2\pi \approx 20$  kHz,

which basically defines the limit of resolution. The first results<sup>99</sup> were obtained for the level  $v''_a = 0, J''_a = 28$  for <sup>23</sup>Na<sub>2</sub> ( $X^1\Sigma_g^+$ ), and they made it possible to measure for the first time the spin-rotational interaction constant  $c$  and to refine the quadrupole interaction constant  $eqQ$ . The characteristic value of the detected hyperfine splitting was of the order of 100 kHz. Exceptional accuracy was achieved in a later paper by this same group<sup>100</sup> by using a dye laser to excite Na<sub>2</sub> ( $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ ),  $J''_a$  from 1 to 29. Some of the results are given in Table IV. A similar method was used in Ref. 206 for I<sub>2</sub> molecules.

## 5. THE EFFECT OF AN EXTERNAL MAGNETIC FIELD ON THE DISTRIBUTION OF ANGULAR MOMENTA

### 5.1. Basic concepts

In the decade after the discovery of the Hanle effect<sup>1</sup> and before the work of Kastler on the optical pumping of atoms,<sup>2</sup> there were few publications on this subject (for more detail, see Ref. 7). The situation changed after the work of Colegrove *et al.*<sup>102</sup> in 1959, when the Hanle effect was interpreted as a special case of the intersection of the Zeeman sublevels of a state in a magnetic field. Later, in the work of Alexandrov, Series, *et al.* the intersection of levels was in turn associated with a more general group of phenomena of the interference of magnetic sublevels, including nondegenerate ones, phenomena such as quantum beats in the case of pulsed excitation,<sup>103,104</sup> the resonance of beats in the case of harmonically modulated excitation,<sup>105,106</sup> phase resonance of beats,<sup>107,108</sup> and other types of resonances; see, for example, Refs. 109 and 110. An exposition of the foundations of these phenomena can be found in monographs of Refs. 9, 15, 16 and reviews of Refs. 3, 4, 111–114. For molecules excited by electrons, the Hanle effect was discussed in Ref. 115 and first recorded<sup>14</sup> in 1969 in the dimers Na<sub>2</sub> ( $B^1\Pi_u$ ). Quantum beats were recorded<sup>116</sup> in 1974 in I<sub>2</sub> ( $B^3\Pi$ ).

The basic features of interference phenomena can be not only completely understood, but they have also been quantitatively described on the basis of the following classical treatment. Each angular momentum  $J$  is associated with

TABLE IV. Landé factors  $g$  of the ground electron state and hyperfine interaction constants ( $eqQ$  is the electric quadrupole,  $c$  the nuclear spin-rotation) of some dimers.

Dimer	State	Landé factor $g, 10^{-3}$	$c, \text{Hz}$	$eqQ, \text{kHz}$
<sup>7</sup> Li <sub>2</sub>	$X^1\Sigma_g^+$	5,9170 [132]		60 [130]
<sup>23</sup> Na <sub>2</sub>	$X^1\Sigma_g^+$	2,4329 [100]	$320 \pm 180$ [190] $242, 9 \pm 1, 5$ [100]	$-423$ [132] $-458, 98$ $-0,000728 J''(J''+1)$ [100] $-158$ [132]
<sup>39</sup> K <sub>2</sub>	$X^1\Sigma_g^+$ $v'' = 1, J'' = 73$	1,4854 [132] $1,24 \pm 0,07$ [142] $1,30 \pm 0,27$ [137] $1,16 \pm 0,15$ [128]	$72 \pm 61$ [191]	
<sup>85</sup> Rb <sub>2</sub>	$X^1\Sigma_g^+$	0,522 [132]		
<sup>85</sup> Rb <sup>87</sup> Rb	$X^1\Sigma_g^+$	0,515 [132]	$249 \pm 35$ ( <sup>87</sup> Rb <sub>2</sub> ) [191]	$-1100$ [132]
<sup>133</sup> Cs <sub>2</sub>	$X^1\Sigma_g^+$	0,298 [132]	$101 \pm 12$ [190]	230 [132]
<sup>130</sup> Te <sub>2</sub>	$XO_g^+$ $v'' = 6, J'' = 52$	$-19,6 \pm 0,8$ [142]		
I <sub>2</sub>	$X^1\Sigma_g^+$ $v'' = 0, J'' = 13 \text{ и } 15$		3,162 [206]	$-2\,452\,583,7$ [206]

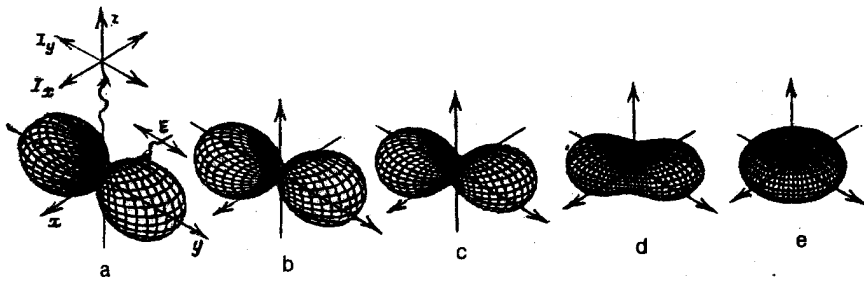


FIG. 8. Change in the distribution of moments of the excited state  $\rho_b(\theta, \varphi)$  due to precession in the magnetic field  $\mathbf{B} \parallel \mathbf{Oz}$  in the case of alignment in  $Q^+$  excitation by a weak light. The values of  $\omega_J / \Gamma_K$  are: a. 0; b. 0.5; c. 1.0; d. 1.5; e.  $\infty$ .

a collinear magnetic moment

$$\mu_J = g_J (\mu_0) [J(J+1)]^{1/2}.$$

The magnetic field  $\mathbf{B}$  causes precession of the angular momentum  $\mathbf{J}$  around  $\mathbf{B}$  with an angular velocity  $\omega_J = g_J \mu_0 \mathbf{B} / \hbar$ . When an ensemble of angular momenta is axially symmetric (that is, it is described by polarization moments  $\rho_Q^K$ , which characterize the so-called longitudinal alignment) in relation to  $\mathbf{B}$ , the field has no effect on the distribution of angular momenta. In other words, this field has no effect on the components of  $\rho_Q^K$  with  $Q = 0$ . If the distribution of  $\mathbf{J}$  is also described by  $\rho_Q^K$  with  $Q \neq 0$ , then in excitation by a short light pulse, the magnetic field has no effect after the pulse on the value of

$$\text{Mod } \rho_Q^K = [(\text{Re } \rho_Q^K)^2 + (\text{Im } \rho_Q^K)^2]^{1/2}, \quad (5.1)$$

but due to precession of the angular momenta, the phase  $\psi$  changes:

$$\text{tg } \psi = \frac{\text{Im } \rho_Q^K}{\text{Re } \rho_Q^K} = \text{tg}(\psi_0 + Q\omega_J t),$$

where  $\psi_0$  is the phase of  $\rho_Q^K$  at the time of excitation. This means that due to the symmetry properties, the angular distribution described by multipole moments  $\rho_Q^K$  in a period  $t_1 = 2\pi/Q\omega_J$  rotates by an angle  $\varphi_1 = 2\pi/Q$  and goes over into itself. Fig. 8 illustrates this.

While the molecules rotate in the magnetic field, relaxation processes are occurring within them, for example, radiative decay at a rate  $\Gamma_K$  according to the rule

$$\text{Mod } \rho_Q^K(t) = \text{Mod } \rho_Q^K(0) \exp(-\Gamma_K t). \quad (5.2)$$

Both processes (Eqs. (5.1) and (5.2)) are independent in the sense that radiative decay has no effect on changes in the phase  $\psi$ . These concepts make it possible to switch to an examination of interference phenomena associated with the coherence of the molecular ensemble.

## 5.2. The Hanle effect

Let us examine excitation by a weak continuous light. In this case, the steady-state distribution of angular momenta in the excited state is created in the following way. The distribution of angular momenta is determined by the ratio of the rates of precession and relaxation  $\omega_J / \Gamma_K$ . Figure 8 shows the distributions of angular momenta of a molecule in an excited state for various  $\omega_J / \Gamma_K$  in  $Q^+$  excitation by a weak linearly polarized light. Figure 13 (below) presents a similar situation for excitation by circularly polarized light propagating along the  $x$  axis.

In linearly polarized excitation the Hanle signal is tra-

ditionally recorded using the degree of polarization in observation along the magnetic field (see Fig. 10). According to Eq. (5.1), the magnetic field has no effect on the total intensity of radiation; it only redistributes it in space. This means that the total number of excited molecules does not depend on the strength of the the  $\mathbf{B}$  field; that is, the volumes of the figures shown in Figs. 8 and 13 are constant. For Fig. 8 the intensity of radiation propagating along the magnetic field  $\mathbf{B}$  does not change; consequently,  $I_y + I_x = \text{const}$ , and it is sufficient to examine the value  $I_y - I_x \sim P$ , which, according to Eq. (3.12), is proportional to

$$I_y - I_x \sim \text{Re } \rho_Q^K(t) = \text{Mod } \rho_Q^K(0) \exp(-\Gamma_K t) \cos(\psi_0 + Q\omega_J t). \quad (5.3)$$

To obtain the expected signal in steady-state excitation and observation one must average the value  $\text{Re } \rho_Q^K(t)$  over time

$$I_y - I_x \sim \overline{\text{Re } \rho_Q^K} = \text{Mod } \rho_Q^K(0) \frac{\Gamma_K \cos \psi_0 + 2\omega_J \sin \psi_0}{\Gamma_K^2 + 4\omega_J^2}. \quad (5.4)$$

For example, when the  $\mathbf{E}$  vector lies in the  $xy$  plane and forms an angle  $\varphi$  with the  $x$  axis,  $\psi_0 = 2\varphi$ . Consequently, if  $\mathbf{E}$  is parallel to the  $y$  axis, we get the traditional Lorentz dependence of the degree of polarization on the magnetic field

$$P = P_0 \frac{1}{1 + 4(g_J \mu_0 B / \hbar \Gamma_K)^2}, \quad (5.5)$$

which makes it possible, if one knows either  $g_J$  or  $\Gamma_K$ , to determine the other value. As an example, Fig. 9 shows the Hanle signal from Ref. 53, which makes it possible to determine the Landé factor given in Table III for  $\text{Te}_2(\text{AO}_v^+)$  molecules. Studies to determine the Landé factors and lifetimes using the Hanle effect method have been carried out for a large number of molecules and radicals. We indicate the first investigations carried out in 1969–1970:  $\text{OH}(\text{A}^2\Sigma^+)$  Ref. 117;  $\text{CO}(\text{A}^1\Pi)$  Ref. 118;  $\text{CS}(\text{A}^1\Pi)$  Ref. 119;  $\text{NO}(\text{A}^2\Sigma^+)$  Ref. 120. Their main goal was to demonstrate

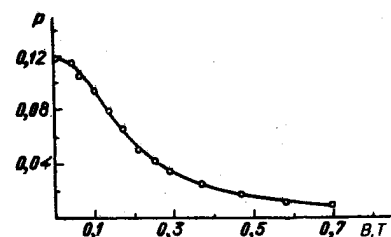


FIG. 9. Hanle effect of the excited level of  $\text{Te}_2(\text{AO}_v^+, 11.53)$  for weak excitation<sup>53</sup> (6.52)  $\rightarrow$  (11.53). (Ref. 53).

the effect and its application to the measurement of lifetimes, in a number of cases in conjunction with the double resonance method for determining  $g_{J'}$ . The problem of finding the Landé factors of rotation levels was solved for  $I_2$  (Refs. 5 and 121),  $Se_2$  (Ref. 25),  $Te_2$  (Refs. 26 and 53) and others.

If the  $E$  vector is in the  $xy$  plane at an angle of  $45^\circ$  to the  $x$  axis, the dependence of the degree of polarization on the magnetic field (Eq. (5.4)) has the dispersion form

$$P = P_0 \frac{g_{J'} \mu_B B / \hbar \Gamma_K}{1 + 4 (g_{J'} \mu_B B / \hbar \Gamma_K)^2}, \quad (5.6)$$

which makes it possible to determine the sign of the Landé factor. This was done for  $Se_2$  (Ref. 122),  $Te_2$  (Refs. 26, 123), and  $K_2$  (Ref. 123) (see below Fig. 15 curve 1). The amplitude of the dispersion signal can be increased somewhat if one changes the recording geometry slightly.<sup>123</sup>

A more complex picture arises when the light used for excitation is rather intense and creates an anisotropic distribution of angular momenta in the molecules in the ground

state as well. The Hanle signal for these conditions was first recorded for  $Na_2$  and  $K_2$  in Refs. 71 and 124. A classical description was given by Ducloy.<sup>32</sup> In Fig. 10 distributions are shown, one above the other, of the angular momenta  $\rho_b(\theta, \varphi)$  of the excited state and  $\rho_a(\theta, \varphi)$  of the ground state for a P, R transition. To construct the figure a steady-state solution of the system of equations given below in section 6 was used. When there is no magnetic field,  $\omega_{J'}/\Gamma_K$ ,  $\omega_{J'}/\gamma_x = 0$ , and light used for excitation creates an anisotropy of  $J$  in both the excited and ground states (see Fig. 10a and also Fig. 5 and its discussion). When the field  $B$  is switched on, depending on the correlation of the signs of the Landé factors  $g_{J'}$  and  $g_{J''}$ , the angular momenta of the ground state  $J_a$  and the excited state  $J_b$  may precess around  $B$  in the same or in opposite directions. What is important here is through what angle, on average, during the lifetime  $\Gamma_K^{-1}$  and  $\gamma_x^{-1}$  do the angular momenta of both states have time to rotate, that is, the correlation of parameters  $\omega_{J'}/\Gamma_K$  and  $\omega_{J'}/\gamma_x$ .

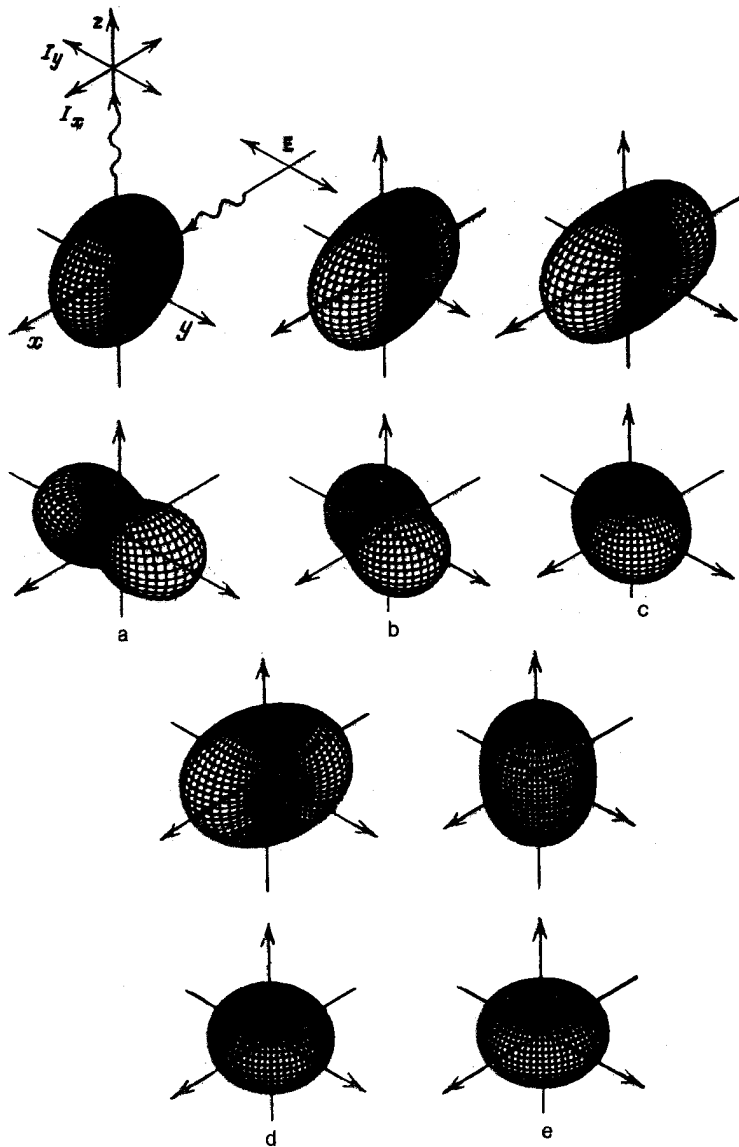


FIG. 10. Distribution  $\rho_a(\theta, \varphi)$  (below) and  $\rho_b(\theta, \varphi)$  (above) for P, R type linearly polarized excitation.  $\Gamma_p/\gamma = 10/3$ ,  $\Gamma_p/\Gamma = 10^{-2}$ . The ratios  $\omega_{J'}/\gamma$  and  $\omega_{J'}/\Gamma$  are respectively equal to: a. zero; b. 1 and 0.05; c. 2.6 and 0.11; d. 10 and 0.46; e. infinitely large.

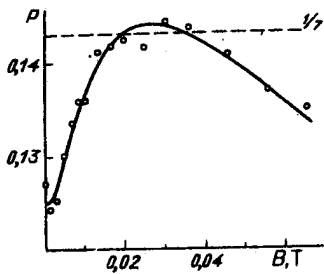


FIG. 11. The same dependence<sup>125</sup> as in Fig. 9 but in a region of lower magnetic fields and for intense pumping ( $\omega \approx 20 \text{ W} \cdot \text{cm}^{-2}$ ,  $\chi = 3$ ). (Ref. 125).

The situation shown in Fig. 10 corresponds to the case when  $g_J, g_{J'} > 0$ ; that is, the signs of the Landé factors are identical and  $\omega_{J'}/\gamma_{J'} = 22\omega_J/\Gamma_K$ . It was assumed that  $\Gamma_K = \Gamma$ ,  $\gamma_{J'} = \gamma$ . If, as before, we make a judgment on the anisotropy of the angular momenta on the basis of the degree of polarization of fluorescence in observation along B, the conditions in Fig. 10 correspond to the dependence  $P(\omega_{J'}/\gamma)$  in Fig. 11, where data from an experiment with  $^{130}\text{Te}_2$  is given.<sup>125</sup> An increase in the degree of polarization at small values of  $\omega_{J'}/\gamma$  reflects the Hanle signal of the ground state, which in our example is more sensitive to the effect of the magnetic field. For large  $\omega_{J'}/\gamma$  a wider signal appears which corresponds to the excited level. Here one fact is noteworthy: When the effect from the ground state has already become prominent ( $\omega_{J'}/\gamma \gg 1$ ) while the effect of the excited state is still weakly manifested ( $\omega_{J'}/\gamma \ll 1$ ), the degree of polarization of fluorescence exceeds  $1/7$ , this value occurring in the case of weak interaction.<sup>17</sup> Such an effect has been observed experimentally<sup>125</sup> and analyzed in detail.<sup>126</sup> Its graphic interpretation can be understood from the discussion of Figs. 5c and 5d in section 4.2. If we turn to Fig. 10, it is clear that when  $\omega_{J'}/\gamma > 1$ , the distribution  $\rho_a(\theta, \varphi)$  approaches a toroidal shape, position (c) in the figure; that is, the anisotropy of angular momenta disappears in the  $xy$  plane; however, as before, the angular momentum  $J_a \parallel Oz$  is singled out. This means there is a decrease in the number of absorbing oscillators with  $d\perp J_a$ , which rotate with the axis of the molecule in the  $xy$  plane. But it is just these oscillators, being excited predominantly along  $E \parallel Oy$  that, due to rapid rotation, transfer the excitation from the  $Oy$  direction (the main contribution to  $I_y$ ) to the  $Ox$  direction (contribution to  $I_x$ ), which in essence means "rotational" depolarization, yielding  $P = 1/7$  in the case of weak excitation. Thus, the anisotropy of angular momenta  $J_a$ , position (c) in the figure, leads to a partial removal of the depolarizing effect of the molecular rotation, which is graphically manifested in a distribution  $\rho_b$ , which is more

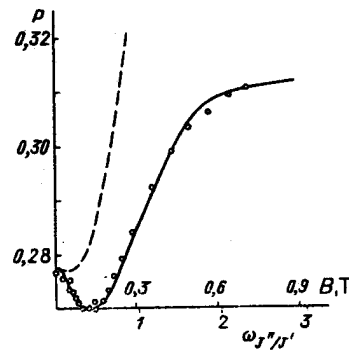


FIG. 12. Experimentally recorded (points) manifestation of the additional structure of the Hanle effect of the lower level of  $K_2(X^1\Sigma_g^+, 1.73)$ . The solid curve is the result of approximation with  $\gamma = 0.35 \mu\text{s}^{-1}$ ,  $\Gamma_p = 2-4 \mu\text{s}^{-1}$ ; the remaining data are from Tables III and IV. The dashed line was calculated from the same parameters<sup>128</sup> but for identical signs of  $g_J$  and  $g_{J'}$ .

"elongated" along  $Oy \parallel E$  compared with the case in Fig. 4b, where there is no optical pumping.

Since the multipole moment  ${}_b\rho_2^2$ , which has a direct effect on the degree of polarization of fluorescence, is linked by the intense light causing excitation with the entire set of moments of the ground state  ${}_a\rho_q^\kappa$ , and, moreover, the total intensity in the direction of the magnetic field,  $I_x + I_y$ , in nonlinear absorption also depends on the magnetic field, the interpretation of a nonlinear Hanle signal in the language of polarization moments is more complex, as is the shape of the signal itself. For example, when  $g_J, g_{J'} < 0$ , that is, when the signs of the Landé factors of the states are different, the dependence  $P(B)$  near  $B = 0$  may exhibit an additional narrow structure caused by the manifestation through  ${}_a\rho_q^4$  of a nonlinear associated moment of order  $\kappa = 6$ , as well as higher orders. Such a structure for Q $\uparrow$  absorption can be seen in Fig. 12. It has been experimentally observed<sup>71, 127, 128</sup> and interpreted<sup>129</sup>, and for states with finite  $J'$ , observations and interpretation can be found in Ref. 134.

The effect of an external magnetic field on fluorescence in the case of circularly polarized excitation and observation is more complex.<sup>130</sup> A picture of the distribution of moments for an oriented ensemble is given in Fig. 13. In this case, the light, along with alignment, creates orientation (that is, a multipole moment of an odd order) of the angular momenta in the upper and lower levels. In orientation of the angular momenta of the ground state one can expect the manifestation in the signal of an octupole orientation as well,  ${}_a\rho_q^3$ . This orientation was recorded, for example, in the studies of Zare *et al.* in collisions of a beam of molecules with a surface.<sup>131</sup>

Let us now turn to the case where the effect of the mag-

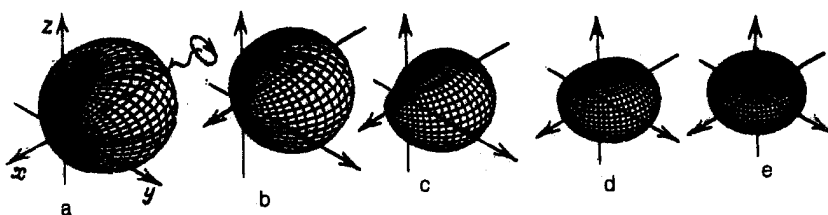


FIG. 13. Precession of the distribution of moments  $\rho_b(\theta, \varphi)$  around a magnetic field  $B \parallel Oz$  for orientation in P $\uparrow$ , R $\uparrow$  excitation by circularly polarized light. The values of  $\omega_{J'}/\Gamma$  are: a. 0; b. 0.5; c. 1.5; d.  $\infty$ .

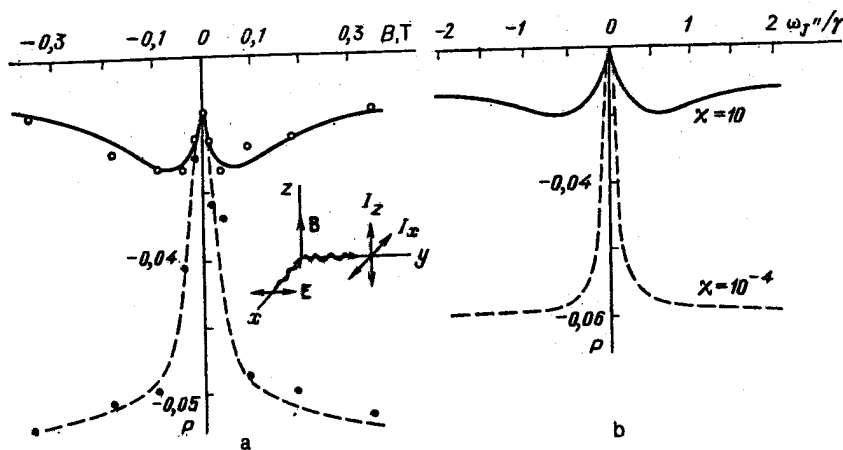


FIG. 14. Changes in the degree of polarization with an increase in the magnetic field in observation from the "end" of the E vector. a. experiment on  $I_2(X'\Sigma_g^+, v''=0, J''=13 \text{ and } 14) \rightarrow (B^3\Pi_u^+, v'=43, J'=12 \text{ and } 16)$ . The dashed line is for weak excitation; b. calculation<sup>162</sup> of  $\omega_J/\gamma = 5\omega_J/\Gamma$ .

netic field is stronger in the excited state, that is  $\omega_J/\Gamma_K \gg \omega_J/\gamma_x$ . Now the magnetic field  $B$  averages the distribution of angular momenta in the excited state much more quickly in the  $xy$  plane than it does in the ground state, and the effect of the ground state is not manifested in the fluorescence observed along  $B$ . However, if one records the degree of polarization of fluorescence "from the end" of the E vector (Fig. 14), that is, along the  $y$  axis, the signal from the ground state will be observed.<sup>134</sup> The data from experiments<sup>124</sup> with  $I_2$  where  $\omega_J/\Gamma_K \gg \omega_J/\gamma_x$ , as well as calculations, are given in Fig. 14.

Let us now determine whether it is possible to obtain the Landé factors of the ground state from the Hanle signal. Earlier, the only method for dimers was the method of magnetic resonance in Ramsay beams, which was used in Ref. 132 to measure the  $g_J$  factors of all alkali dimers (see Table IV). The Hanle effect of the ground state was in essence ill suited for the determination of  $g_J$  because one needed to measure separately the rate of relaxation  $\gamma_x$ , which in itself is not easy (see section 4). A certain opportunity is provided here by the use of the conditions in Eq. (4.7) for transit relaxation, which was implemented in Ref. 128. Results were obtained for  $K_2(X'\Sigma_g^+)$ , and these are given in Table IV. It is of interest to determine the sign of the  $g_J$  factor. The magnetism of a diamagnetic ground state is of a gyromagnetic nature (see Refs. 27-29, 35, 132, 133 and the references therein); it is caused by an electronic contribution and the rotation of nuclei. In the case of a dominant electronic

contribution the sign is negative, as for  $Te_2(XO_g^+)$  (see Table IV). If the rotation of nuclei is dominant, then the sign is positive, as in alkali dimers. The problem of determining the sign was solved<sup>123</sup> by recording the "dispersion" contours of Eq. (5.6). From the examples given in Fig. 15 it is clear that for  $K_2$ , where  $g_J \cdot g_{J'} < 0$ , the nonlinear Hanle signal of the ground state leads to a large curvature of curve 2 compared with curve 1. For  $Te_2$ , where  $g_J \cdot g_{J'} > 0$ , an additional narrow structure is manifested, curve 3.

The signals of the intersection of levels makes it possible, if one knows  $g_J$ , to determine the relaxation constants  $\gamma$  and cross sections  $\sigma$  for the ground state (Refs. 71, 124, 125, 127, 128, and 135). Due to the presence of a strong light field which mixes  $a\rho_q^x$ , they cannot be correlated with the relaxation of polarization moments of a certain order. At the limit of a weak linearly polarized excitation, when speaking of traditional signals, according to Eq. (5.4) we can determine the rate of relaxation of alignment  $\Gamma_2$ . It is more complicated to determine the relaxation of orientation  $\Gamma_1$ , because when there is excitation by a circularly polarized light, alignment also arises. For this, one can use excitation by a light with given parameters of ellipticity and beam direction.<sup>48</sup>

Thus, the nonlinear signals of the intersection of levels, including the ground state of molecules, demonstrate the disruption of their polarization by an external field, and make it possible to determine the ratio of the relaxation constants to the Landé factor of the vibration-rotation level from which absorption occurs.

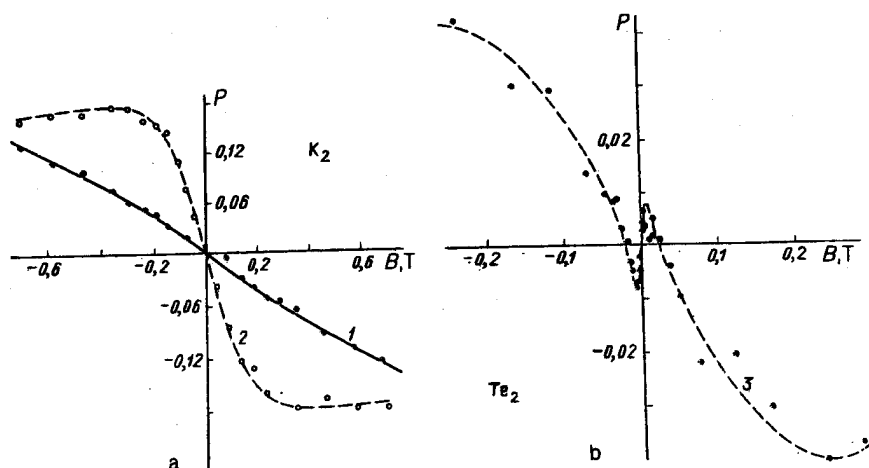


FIG. 15. Recorded "dispersion" Hanle signals<sup>123</sup>: 1. for  $K_2$ , excitation  $(X'\Sigma_g^+, 1.73) \rightarrow (B^1\Pi_g, 8.73)$ ,  $\chi \ll 1$ ; 2. the same for  $\chi = 3.0$ ; 3.  $^{130}Te_2$ , excitation  $(XO_g^+, 1.132) \rightarrow (AO_u^+, 11.131)$ .



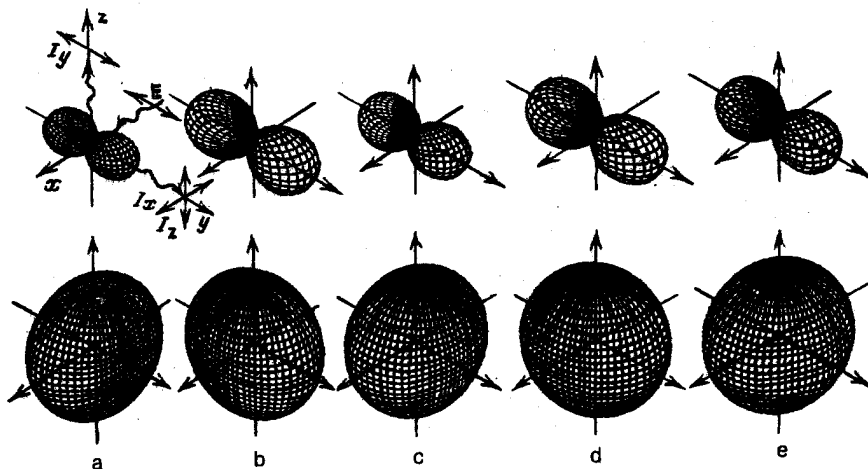


FIG. 16. Change with time ("pulsations") of distribution  $\rho_b$  of the moments of an excited level (above) due to precession around  $B \parallel Oz$  of the distribution  $\rho_a$  of the moments of the lower state created by a  $\delta$  pulse (below) for  $\omega_J/\gamma = 5$ . a.  $\gamma t = 0$ ; b.  $\gamma t = \pi/10$ ; c.  $\gamma t = \pi/5$ ; d.  $\gamma t = 3\pi/10$ ; e.  $\gamma t = 2\pi/5$ .

### 5.3. Pulse excitation

Let us now turn to the case where the excitation is caused by a light pulse whose duration is much shorter than the characteristic relaxation times. Then there is simultaneous decay and precession of the distribution  $\rho_Q^K(t)$  according to Eqs. (5.1) and (5.2), and this is described by Eq. (5.3). If we track, using the geometry of Fig. 16, the development over time of the intensity of fluorescence, then, for example, for  $I_x$ , we can obtain from Eq. (3.12)

$$I_x \sim k_{1b}\rho_0^0 + k_{2b}\rho_0^2 + k_{3b} \operatorname{Re} \rho_0^2 \\ = k_{1b}\rho_0^0 + k_{2b}\rho_0^2 + k_{3b} \operatorname{Mod} \rho_0^2(0) \exp(-\Gamma_2 t) \cos(\psi_0 + 2\omega_J t). \quad (5.7)$$

Equation (5.7) demonstrates the manifestation of quantum beats of the polarization moment  ${}_b\rho_2^2$  in the intensity of radiation, which consists of the superposition of harmonic oscillations with frequency  $2\omega_J$ , on the factor of exponential decay  $\exp(-\Gamma_2 t)$ . As we can see, this phenomenon has the same basis as the Hanle effect—the competition of the precession of the distribution  $\rho_b(\theta, \varphi)$  around the field  $B$  with relaxation, but there is also a significant difference: a phase-synchronizing single moment of excitation  $t_0$  (it is assumed that  $t_0 = 0$ ). We will not discuss the phenomenon of beats in more detail here, but instead refer the reader to the pioneering studies and reviews (Refs. 3, 15, 16, 103, 104, 109, 110, and 114). We turn now to the manifestation of the effect from the ground state of the molecules.<sup>136,137</sup> To do this, we express  ${}_b\rho_Q^K(t)$  using the multipole moments of the lower state<sup>137</sup>  ${}_a\rho_q^K(t)$

$${}_b\rho_Q^K = \frac{\Gamma_p}{\Gamma_K - iQ\omega_J} \sum_{\nu q} {}_q^K D_q^K {}_a\rho_q^K(t). \quad (5.8)$$

The coefficients  ${}_q^K D_q^K$  are real quantities. To separate reliably the signals of quantum beats of the ground and excited state, one must satisfy the conditions  $\Gamma_K \gg Q\omega_J, \gamma_x$ . Then

$$\operatorname{Re} {}_b\rho_Q^K(t) = \frac{\Gamma_p}{\Gamma_K} \sum_{\nu q} {}_q^K D_q^K \operatorname{Re} {}_a\rho_q^K(t). \quad (5.9)$$

The distribution of angular momenta of the lower level created by the  $\delta$  pulse at time  $t_0 = 0$  develops with time on the scale  $t \sim \gamma_x^{-1}$

$$\operatorname{Re} {}_a\rho_q^K(t) = \delta_{\nu 0} - (\delta_{\nu 0} - {}_a\rho_q^K(0)) \exp(-\gamma_x t) \cos q\omega_J t. \quad (5.10)$$

It is clear from Eqs. (5.9) and (5.10) that oscillations of the moments of the ground state  ${}_a\rho_q^K$  with a frequency  $q\omega_J$  are manifested in the fluorescence through  ${}_b\rho_Q^K$ . The amplitude of the oscillations decreases on the background of an increase in the signal due to thermalization at the rate  $\gamma_x$ . The manifestation of beats from the ground state can be graphically represented analogously to the Hanle effect as a transition of the distribution  $\rho_a(\theta, \varphi)$  into itself (see Fig. 16) with precession around  $B$  with a period  $t_1 = 2\pi/q\omega_J$ , which leads to a periodic change in the number of molecules which are capable of absorption. This is manifested as a periodic increase in the number of excited molecules or the pulsation of the volume of the corresponding figures of Fig. 16 (upper illustrations).

A graphic illustration of the expressions for observed signals<sup>137</sup>  $I(t)$  for linearly polarized excitation is given in Fig. 17. It is clear that beats with a frequency  $2\omega_J$  are manifested and are dominant in  $I_x$  and  $I_y$ . In  $I_z$ , only "hexadecapole" beats with a frequency  $4\omega_J$  are manifested.

In experimental observation of quantum beats from the

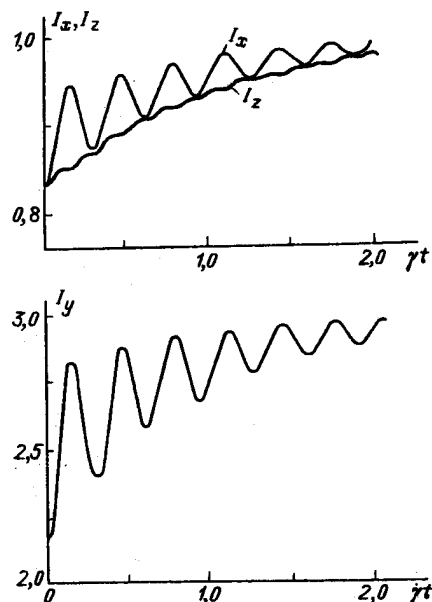


FIG. 17. Calculated signals<sup>137</sup> of quantum beats of the ground state for  $\omega_J/\gamma = 10$  (geometry as in Fig. 16).

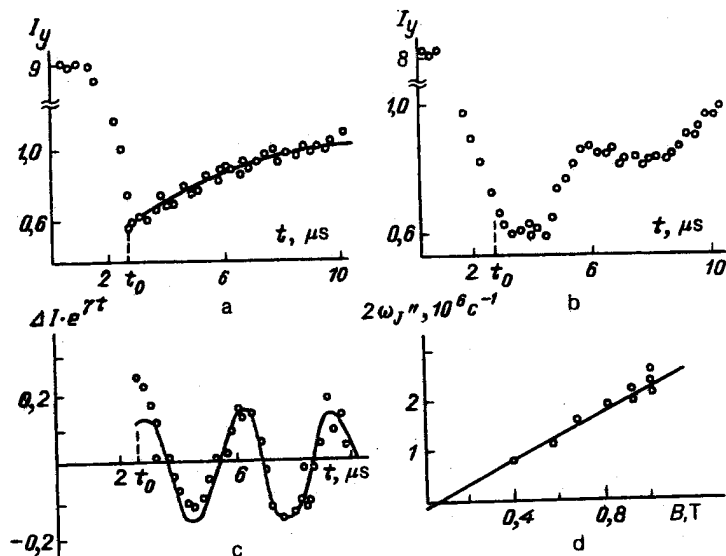


FIG. 18. Experimentally recorded signals of quantum beats in  $K_2(X^1\Sigma_g^+, 1.73)$  in the transition process. a. field switched on; b.  $B = 0.816$  T; c. difference signal with compensation of the attenuation of beat amplitudes; d. dependence of  $\omega_{J''}$  on  $B$ . (Ref. 136).

ground state of molecules the main problem is the need to use a large magnetic field. This is associated with the small  $g_{J''}$  factors of the diamagnetic states ( $10^{-5}$  to  $10^{-4}$ ; see Table IV) and the need to manifest a sufficient number of oscillation periods on the scale of  $\gamma_x^{-1}$ . Figure 18 gives an example of signals which were recorded<sup>136</sup> for  $K_2(X^1\Sigma_g^+)$ . The laser beam (623.8 nm) was modulated with a depth of 0.8–0.9 in the form of pulses with a duration  $\Delta t \approx 1 \cdot 10^{-6}$  to  $2 \cdot 10^{-6}$  s. The kinetics of the transition process in the radiation ( $I_y$  component) excited by the "substrate" after the pulse cut-off are shown in Fig. 18a. In Fig. 18b where a magnetic field  $B = 0.816$  tesla directed along the  $z$  axis is switched on one can differentiate the oscillations. The signal in Fig. 18c was obtained by subtracting two signals and multiplying by the factor  $\exp(\gamma_x t)$ , which compensates for attenuation of the amplitude. In this figure one can determine the beat frequency  $\omega_{J''}$ . It is clear that it is desirable to decrease the period of beats to obtain a clearer manifestation of them; however, the capabilities of the electromagnet used were insufficient. Nonetheless, the dependence of  $\omega_{J''}$  on  $B$  (Fig. 18d) leads to a Landé factor for  $v'' = 1, J'' = 73$  equal to  $g_{J''} = (1.30 \pm 0.27) \cdot 10^{-5}$ . The main advantage of the method is recording in the region of weak excitation, that is, when the effect of the strong light pulse has ended. In many cases,<sup>137</sup> an approximation of the signal of Fig. 18b in the following form is satisfactory

$$I(t) = I(t \rightarrow \infty) - C_1 \exp(-\gamma t) + C_2 \cos(2\omega_{J''}t + \psi_0) \exp(-\gamma t). \quad (5.11)$$

In solving the problem of the increase in  $\omega_{J''}/\gamma_x$ , when the error is decisively decreased, this method is the optimal method for measuring the Landé factors of ground state levels with a fixed vibration and rotation number.

#### 5.4. Resonance of beats

Another variation on the recording of beats of the ground state of diatomic molecules through fluorescence was proposed in Ref. 138, and consists of harmonic modulation with a frequency  $\Omega_1$  of the laser beam used for excitation when the rate of absorption varies according to the rule

$\Gamma_p = \Gamma_{p0}(1 - \varepsilon \sin \Omega_1 t)$ . If the molecules are situated in the magnetic field  $B$ , then near  $\Omega_1 = qg_{J''}\mu_0 B/\hbar$  one will observe a resonance change in the recorded fluorescence. The value  $q$  here is again linked with the symmetry of the distribution of angular momenta  $J_a$ . Actually, when  $\Omega_1$  coincides with the frequency of transition of the distribution  $\rho_a$  into itself in precession around  $B$  (see Fig. 16), one should expect a more efficient excitation (something like the stroboscopic effect) which causes the signal of beat resonance. It is noteworthy that, in contrast to the situation in the excited state in excitation by weak light (Refs. 15, 16, 105, 106, 109, and 110), here the effect is of a nonlinear character, and thus is manifested in a recording averaged over time.

The shape of the signal recorded<sup>139,141</sup> for the same test object,  $K_2(X^1\Sigma_g^+)$  is shown in Fig. 19. Although the origin of the effect is completely understood and is, in the simplest approximation, described by analytical expressions,<sup>138</sup> the

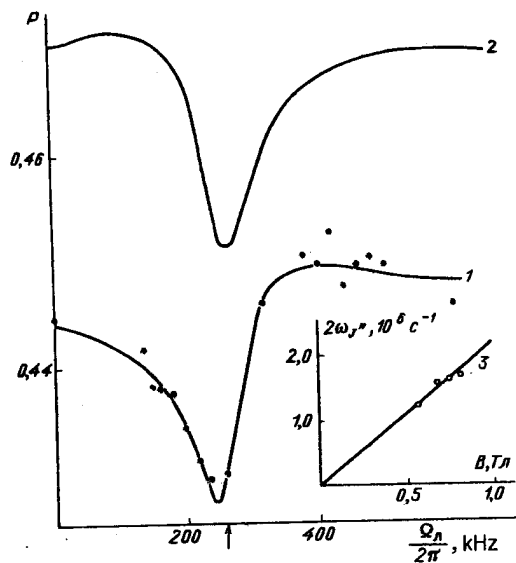


FIG. 19. Signals of the beat resonance of  $K_2(X^1\Sigma_g^+, 1.73)$  in the form of the dependence of the degree of polarization of fluorescence on the frequency of modulation of the excitation  $\Omega_1$  in a constant magnetic field of 0.589 T. The arrow indicates the value  $\Omega_1 = 2\omega_{J''}$ . (Ref. 142).

accuracy is insufficient because the situation is noticeably more complex (compared to quantum beats). This is due to the presence of a pumping field which causes a nonlinear shift in the position of the resonance and a change in curve shape. Efforts exerted in Refs. 140–142 made it possible, on the basis of classical concepts, to describe with sufficient accuracy the shape of the recorded signal (the solid curve in Fig. 19). This was done by using  $\omega_{J'}$  as one of the adjustment parameters. The dependence  $\omega_{J'}(B)$  which was determined in this way yielded a Landé factor  $g_{J'} = (1.24 \pm 0.07) \cdot 10^{-5}$ . The result for  $^{130}\text{Te}_2(\text{XO}_g^+, 6.52)$ , which was obtained using the beat resonance method<sup>138</sup> and following the interpretation of results as in Ref. 142, yielded a value,  $g_{J'} = -(19.6 \pm 0.8) \cdot 10^{-4}$  (see Table IV).

We note an interesting characteristic: In Ref. 139 a hexadecapole signal of the beat resonance was recorded (with  $q=4$ ) in the form of a small maximum in the region  $\Omega_1 = 4\omega_{J'}$ . In the description of the effect, as in the case of a nonlinear Hanle signal, it is important to consider properly the signs of the Landé factors  $g_{J'}$  and  $g_{J''}$  of the states which are combining. Nonlinear parametric, phase, and relaxation resonances in molecules were examined in Ref. 143; however, they were not experimentally recorded. The basic problems here are again associated with large magnetic fields (compared to atomic systems), and the need to resolve the vibration-rotation structure. In the resolution of these difficulties, nonlinear methods for the interference of nondegenerate states make it possible to determine independently the Landé factors and the rates of relaxation of the polarization moments.

### 5.5. Polarization spectroscopy

Up until now we have made judgments about the polarization (orientation and alignment) of the angular momenta of molecules in the excited and ground states based on fluorescence. If our goal is to study the ground state of molecules, then this approach should be regarded as being not quite direct. From the very beginning the absorption of light transfers the molecule into an excited state where it may experience various effects (collisions, the effect of external fields, etc.). It is only after this that de-excitation occurs, from which we make judgments about the ground state of molecules.

Obviously, if we record not the fluorescence, but the absorption of light variously polarized, one can directly obtain information about the distribution of angular momenta of the ground state of molecules. Actually, if we ignore induced transitions, the value of the coefficient of absorption  $\alpha$  depends only on the polarization of light  $\hat{E}$  and on the polarization of the angular momenta of the ground level of the molecule.<sup>144</sup>

$$\alpha(\hat{E}) = A \sum_x (-1)^{x+\Delta} (2x+1)^{1/2} C_{1\Delta 1, -\Delta}^{x0} \sum_q (-1)^q \Phi_q^x(\hat{E}) \rho_{-q}^x. \quad (5.12)$$

However, measurement of the absorption of light by molecules with a given vibration-rotation level is a rather complicated task which requires large concentrations of molecules and narrow laser lines; thus, the fluorescence method is much more sensitive than the absorption method, at least in the visible part of the spectrum. The main prob-

lems are associated with the need to record small changes in intensity against a background of a large transient signal.

Beginning with the work of Hänsch, Schawlow *et al.*<sup>97,98,145</sup> these drawbacks were successfully overcome using the method of polarization spectroscopy. The essence of the method is as follows. Intense laser radiation polarizes a rarified gaseous medium of atoms or molecules; that is, the medium acquires an induced dichroism and gyrotropy. If the medium is placed between crossed polarizers and transilluminated by a weak probe wave, only that part of the wave which will be defined by the anisotropic properties of the gas will pass through the system.<sup>146</sup> The method makes it possible to record the spectrum with high resolution and a good signal to noise ratio in both atoms (Ref. 97) and molecules (Refs. 96, 98, 145, and 146). The use of polarization spectroscopy makes it possible to measure the rate of relaxation of polarization moments of different orders; see, for example, Refs. 147 and 148. Let us examine how an external magnetic field which changes the distribution of angular momenta of particles affects the signals of polarization spectroscopy. These experiments were done on Na atoms in Ref. 149. The experiment can be designed so that when the medium is probed by light with a broad spectral content in a situation when  $\Gamma_p \ll \Gamma_K$ , the polarization spectroscopy signal will be determined exclusively by absorption. The crossed polarizers make it possible to measure the useful signal against a small background of transient light. This small background is due to the fact that the amplitude of the polarization signal is the greatest amplitude, and it is easiest to interpret it in the case where the angle between the axes of the polarizers differs from a right angle by a small amount  $\epsilon$ .<sup>77,144</sup> Let there be a strong field  $E_S$  which polarizes the angular momenta of molecules in the ground state and is linearly polarized along the  $y$  axis. Let there also be a weak probe field  $E_p$ , which propagates along the  $z$  axis and is polarized at an angle  $\pi/4$  to the  $x$  axis (Fig. 20). In this case the signal beyond the analyzer crossed with  $E_p$  will be defined by the difference between the coefficients of absorption  $\alpha_x - \alpha_y$  for light which is polarized along the  $x$  and  $y$  axes. This result can be easily understood. As a result of the effect of the strong wave of  $E_S$ , the number of molecules with an angular momentum directed along these axes is different (see Figs 5b and 5d), so the components  $E_{Vx}$  and  $E_{Vy}$  of wave  $E_p$  are absorbed differently. As a result, there is a rotation of the plane of polarization of the probe wave and the signal  $I_p$  appears. Its value can be calculated as<sup>144,150,151</sup>

$$I_p \sim \frac{\epsilon^2}{4} + \epsilon \frac{l}{4} (\alpha_x - \alpha_y) = \frac{\epsilon^2}{4} + \epsilon \frac{l}{4} U_\Delta \text{Re} \rho_2^2, \quad (5.13)$$

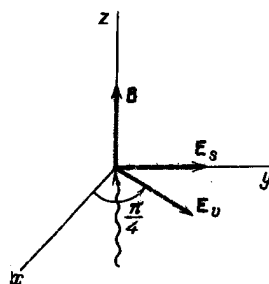


FIG. 20. Geometry of an experiment in polarization spectroscopy.

where  $l$  is the path length of the probe beam in the polarized gas, and  $U_{\Delta}$  is a coefficient which depends on the type of molecular transition. It is assumed that the dependence of  $\text{Re} a \rho_2^2$  on time and the external magnetic field coincides with the analogous dependence (Eq. (5.3)) for the excited state  $b$ , that is,

$$\text{Re} a \rho_2^2(t) = \text{Mod} a \rho_2^2(0) \exp(-\gamma_2 t) \cos(2\omega_J t + \psi_0). \quad (5.14)$$

Thus, the methods of polarization spectroscopy can be used for the ground state of molecules to record all the types of signals examined earlier in weak excitation of the excited state, that is, the kinetics of relaxation after the pulse of a strong wave, quantum beats beat resonance, and the Hanle effect. Naturally, one should not forget that the calculation of polarization moments  $a \rho_2^2$  for the ground state is more complex than the calculation of  $b \rho_2^2$  in weak excitation. The generation of  $a \rho_2^2$  is associated with the nonlinear interaction of an  $E_S$  wave with molecules in the ground state, and is described by a system of equations which is given in the following section. When one is studying the beat signals after pulse excitation, the multipole moment created by the strong pulse,  $a \rho_2^2$ , then evolves "freely"; thus, its relaxation at a rate  $\gamma_2$  and precession in the magnetic field is completely described by Eq. (5.14)

Reference 144 examined other possible variations of the geometry of designing experiments to study molecules using polarization spectroscopy methods. One can only regret that up until now the possibilities of polarization spectroscopy for the experimental study of molecules have only been used episodically and mainly to decipher spectra.

## 6. EQUATIONS OF MOTION OF POLARIZATION MOMENTS FOR ARBITRARY $J$

For a more detailed analysis of experiments which use aligned and oriented (polarized) molecules in the ground state and excited state, we use a quantum mechanical system of equations of motion for polarization moments  $\varphi_q^x$  and  $f_Q^K$  of the lower and upper level, between which a transition is excited. These equations describe with maximum detail the coefficients which characterize the angular part of the interaction and the effect of an external field. At the same time the dynamic parameters are noticeably simplified ( $\Gamma_p$ ,  $\Gamma_K$ ,  $\gamma_x$  etc.), which is possible when one assumes pumping by light with a broad spectral content. The effect of the monochromaticity of excitation under nonlinear conditions in optical pumping is rather complex, and we refer the reader to special sources; see for example, Refs. 24, 63, 64, 66. The equations are actually written for two states linked by absorption, taking into account the approximations that have been discussed in section 4.

The current view of the generation of optical pumping of atoms and molecules is mainly summarized in Refs. 18, 32, 45, 61, and 152-154. In our survey we will trace this ideology, taking into account some features for diatomic molecules. In the presence of an external magnetic field  $B$  directed along the  $z$  axis the system of equations based on the model discussed in section 4 has the form<sup>155</sup>

$$\begin{aligned} \dot{f}_Q^K &= \Gamma_p \sum_{x,x'} \Gamma^{xx'} \{ \Phi^{(x)} \otimes \varphi^{(x')} \}_Q^K \\ &+ 2i\omega_S \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{x,K'} {}^K A_{1+}^{xx'} \{ \Phi^{(x)} \otimes f^{(K')} \}_Q^K \\ &- \Gamma_p \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{x,K'} {}^K A_{1+}^{xx'} \{ \Phi^{(x)} \otimes f^{(K')} \}_Q^K - (\Gamma_K - iQ\omega_J) f_Q^K, \end{aligned} \quad (6.1a)$$

$$\begin{aligned} \dot{\varphi}_q^x &= -\Gamma_p \sum_{x,x'} A_{1+}^{xx'} \{ \Phi^{(x)} \otimes \varphi^{(x')} \}_q^x \\ &+ 2i\omega_S \sum_{x,x'} A_{1+}^{xx'} \{ \Phi^{(x)} \otimes \varphi^{(x')} \}_q^x \\ &+ \Gamma_p \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{x,K} F_1^{xK} \{ \Phi^{(x)} \otimes f^{(K)} \}_q^x - (\gamma_x - iq\omega_J) \varphi_q^x \\ &+ \Gamma_{J'J''} C_x \delta_{Kx} \delta_{Qq} f_Q^K + \lambda_q^x \delta_{x0} \delta_{q0}. \end{aligned} \quad (6.1b)$$

These equations generalize the approaches used earlier to describe the optical pumping of atoms and molecules (Refs. 134, 138, 152-154). The first term in both equations describes the absorption of light at a rate  $\Gamma_p$ , which leads to the generation of alignment and orientation of molecules in the ground and excited states. The second term describes the effect of a dynamic Stark effect, which leads to a shift in the frequency of the transition by  $\omega_S$ , which is nonzero when the center of the line of excitation does not coincide with the center of the line of absorption (Refs. 152, 153, 156, 157). The third term is the induced emission of light. The fourth term describes the relaxation of polarization moments with rates  $\Gamma_K$ ,  $\gamma_x$  and how the external magnetic field affects it. The next to the last term in Eq. (6.1b) describes the probability, which is small, but nonetheless present, of inverse spontaneous transitions. The last term describes the change in the occupancy of the lower level due to the interaction with the thermostat.

The coefficients  ${}^K F_1^{xx}$ ,  ${}^K F_1^{xK}$ ,  ${}^x A_{1\pm}^{xx'}$ ,  ${}^K A_{1\pm}^{xK'}$  and  $C_x$  take into account the conservation of angular momentum in the optical transition, and have the form

$${}^K F_1^{xx} = \frac{\Pi_{J'}^2 \Pi_{Kx}^2}{\Pi_{J''}^2} (-1)^{x+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ x & J'' & J'' \end{Bmatrix}, \quad (6.2)$$

$$\begin{aligned} &{}^x A_{1\pm}^{xx'} \\ &= \frac{1 \pm (-1)^{x+x'}}{2} \frac{\Pi_{J'}^2 \Pi_{x'}^2}{\Pi_x} (-1)^{J'-J''+x'} \begin{Bmatrix} x & X & x' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J'' \end{Bmatrix}, \end{aligned} \quad (6.3)$$

$$C_x = (-1)^{J'-J''+x+1} \Pi_{J''} \begin{Bmatrix} J'' & J'' & x \\ J' & J' & 1 \end{Bmatrix}, \quad (6.4)$$

where

$$\Pi_{ab\dots} = [(2a+1)(2b+1)\dots]^{1/2}.$$

The coefficients  ${}^K A_{1\pm}^{xK'}$ ,  ${}^x F_1^{xK}$  are obtained from  ${}^x A_{1\pm}^{xx'}$ ,  ${}^K F_1^{xx}$  by changing the places of  $J''$  and  $J'$  in Eqs. (6.2) and (6.3). The quantities in braces are  $6j$  and  $9j$  symbols. The irreducible tensor derivative was defined as

$$\{ \Phi^{(x)} \otimes f^{(K)} \}_q^x = \sum_{\xi, Q} C_{x\xi K Q}^{xq} \Phi_{\xi}^x f_Q^K. \quad (6.5)$$

The formulas which make it possible to calculate the values of the components of the D'yakonov tensor  $\Phi_{\xi}^x$  for various polarizations and propagation directions of the laser beam were obtained in Refs. 45 and 48. The quantities  $\Gamma_p$  and  $\omega_S$

describe the dynamic part of the probability of optical transition<sup>152,153</sup>

$$\Gamma_p = \frac{2\pi}{\hbar^2} |\langle J' \| \hat{d} \| J'' \rangle|^2 i(\omega_0), \quad (6.6)$$

$$\omega_s = \frac{1}{\hbar^2} \text{V.p.} \int \frac{|\langle J' \| \hat{d} \| J'' \rangle|^2}{\omega_l - \omega_0} i(\omega_l) d\omega_l;$$

Here,  $\langle J' \| \hat{d} \| J'' \rangle$  is the reduced matrix element of the transition  $J'' \rightarrow J'$  (see Fig. 2),  $\omega_l$  is the frequency of laser radiation which has a spectral density of intensity  $i(\omega_l)$ ,  $\omega_0$  is the resonance frequency of the transition.

The pumping beam initiates fluorescence with a polarization described by the tensor  $\Phi_\xi^K$  in the transition  $b \rightarrow c$  of a molecule from level  $(\alpha', \nu', J')$  to level  $(\alpha'', \nu'', J'')$  (see Fig. 2). The fluorescence has an intensity<sup>45</sup>

$$I = I_0 \sum_{K=0}^3 \Pi_K^2 \begin{Bmatrix} 1 & 1 & K \\ J' & J' & J'' \end{Bmatrix} \sum_{K=0}^Q (-1)^Q f_Q^K \Phi_{-Q}^K. \quad (6.7)$$

When  $J', J'' \sim 100$ , there are certain problems in solving the system of equations in Eq. (6.1) due to the large number of coupled equations. Since  $0 < K < 2J'$ ,  $0 < \kappa < 2J''$ , and  $-K < Q < K$ ,  $\kappa < q < \kappa$ , their total number is equal to  $(2J' + 1)^2 + (2J'' + 1)^2$ . To solve such a large system for  $\Gamma_p/\Gamma_K$ ,  $\Gamma_p/\gamma_\kappa$ ,  $\omega_s/\Gamma_K$ ,  $\omega_s/\gamma_\kappa < 1$ , one can expand  $\varphi_Q^K, f_Q^K$  into a power series in these parameters. Although as a rule this approach does not make it possible to obtain a sufficiently accurate description of the signals, it is very useful since it makes it possible to arrive at visible analytical connections between the calculated quantities being evaluated. At large parameter values, the system of equations in Eq. (6.1) should be solved numerically. In this case, taking into account that the observed fluorescence signal (Eq. (6.7)) is directly affected only by  $f_Q^K$  of order  $K < 2$ , one can limit the number of polarization moments included in the examination. So, for  $\Gamma_p/\Gamma_K$ ,  $\Gamma_p/\gamma_\kappa$ ,  $\omega_s/\Gamma_K$ ,  $\omega_s/\gamma_\kappa \sim 10$ , the solution obtained is rather accurate for calculation of moments of order  $K, \kappa < 10$  (Ref. 88). A more detailed method for numerically solving the system of equations in Eq. (6.1) is examined in Ref. 88.

Now let us turn to the manifestation of a dynamic Stark effect in the optical pumping of molecules. The most interesting manifestation of this effect is found in the excitation of molecules with linearly polarized light. This effect was examined in Refs. 158 and 159 using a model of dipole oscillators. In this case, due to the effect of the dynamic Stark effect, there is a transition of the alignment created by the light into orientation, which causes the appearance in the fluorescence of a nonzero circular polarization of radiation.

As an example let us examine absorption in the transition  $J'' = 1 \rightarrow J' = 2$ . Let the vector of the light wave  $E$  be orthogonal to the external magnetic field  $B$ . We assume that this frequently occurs in dimers<sup>160</sup> and that  $\Gamma_K = \Gamma \gg \Gamma_p \gtrsim \gamma_\kappa = \gamma$ . Then, due to the dynamic Stark effect in the ground state of the molecule there arises a longitudinal component of the orientation  $\varphi_0^1$ . In the second approximation, expanding  $\varphi_0^1$  in terms of a small parameter, we get<sup>155</sup>

$$\varphi_0^1 = \frac{\sqrt{2}}{108} \frac{\omega_s \Gamma_p}{\gamma} \frac{\omega_{J''}}{\gamma^2 + 4\omega_{J''}^2}. \quad (6.8)$$

The same light used for excitation links  $\varphi_0^1$  with the longitudinal orientation of the excited level, which has a direct effect on the radiation signal.

$$f_0^1 = \frac{\Gamma_p}{\Gamma} \frac{1}{\sqrt{3}} \varphi_0^1 = \frac{\sqrt{6}}{324} \frac{\omega_s \Gamma_p}{\gamma \Gamma} \frac{\omega_{J''}}{\gamma^2 + 4\omega_{J''}^2}. \quad (6.9)$$

In this case, in observation from the end of the vector of the magnetic field, circularly polarized radiation is generated. The difference in the intensities of right-handed ( $r$ ) and left-handed ( $l$ ) polarization in the transition  $J'' = 2 \rightarrow J' = 1$  is equal to

$$I_r - I_l \sim \frac{3}{\sqrt{30}} f_0^1,$$

and in the transition  $J'' = 2 \rightarrow J' = 3$  to

$$I_r - I_l \sim \frac{2}{\sqrt{30}} f_0^1.$$

In order for there to be transverse as well as longitudinal orientation of the molecular ensemble, that is, the component  $\varphi_{\pm 1}^1$ , the angle between the  $E$  vector of the light and the magnetic field  $B$  must differ from 0 and  $\pi/2$  (Ref. 155).

For states with a large angular momentum the manifestation of the effect is not as clear, and at the limit  $J'' \rightarrow \infty$  it disappears.<sup>155</sup> However, the effect may remain noticeable at values of  $J'' \approx 20$  and above.<sup>155</sup> Thus, Fig. 21 shows a computer-calculated dependence of the degree of circular polarization  $C$  on the value of  $\omega_{J''}/\gamma$  for the well-studied transition ( $J'' = 18$ )  $\rightarrow$  ( $J' = 17$ )  $\rightarrow$  ( $J'' = 16$ ) in  $\text{Na}_2$  for excitation by the 632.8 nm line of a He-Ne laser.<sup>163</sup> In the calculations it was assumed that  $\gamma_\kappa = \gamma = 0.3 \mu\text{s}^{-1}$ ,  $\Gamma_K = \Gamma = 83.3 \mu\text{s}^{-1}$ ,  $\Gamma_{J'J''} = 0.83 \mu\text{s}^{-1}$ ,  $\omega_{J'}/\omega_{J''} = -1$ . It is clear that in the case where  $\Gamma_p = \omega_s$ , exceeds by only severalfold the rate of relaxation in the ground state  $\gamma$ , there arises a degree of circular polarization of the radiation which exceeds 0.01, which one should be able to measure reliably in an experiment.

Finally, one should touch on the question of the possibility of obtaining in an experiment a noticeable (compared to  $\Gamma_p$ ) value of the Stark shift  $\omega_s$ . From the definitions of  $\Gamma_p$  and  $\omega_s$  we obtain

$$\frac{\omega_s}{\Gamma_p} = \frac{1}{2\pi} \text{V.p.} \int \frac{i(\omega_l) d\omega_l}{(\omega_l - \omega_0) i(\omega_0)}. \quad (6.10)$$

If it is assumed that the shape of the excitation line is Lorentz-

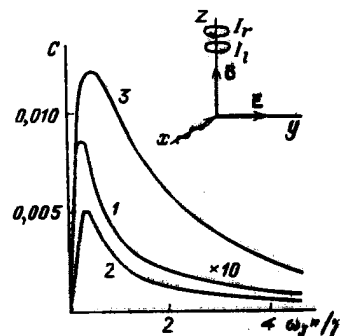


FIG. 21. Manifestation of the degree of circularity  $C$  in linearly polarized excitation. In the calculation it was assumed that: 1.  $\Gamma_p = \omega_s = 0.3 \mu\text{s}^{-1}$ ; 2.  $\Gamma_p = \omega_s = 1.0 \mu\text{s}^{-1}$ ; 3.  $\Gamma_p = \omega_s = 3.0 \mu\text{s}^{-1}$ .

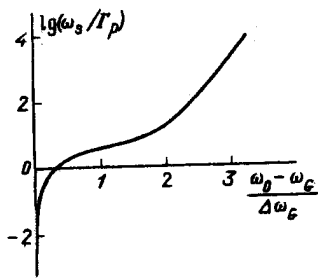


FIG. 22. Dependence of  $\log(\omega_s/\Gamma_p)$  on the ratio  $(\omega_0 - \omega_G)/(\Delta\omega_G)^{-1}$  where the notation corresponds to the contour  $i(\omega) = i_0 \exp[-(\omega - \omega_G)^2/\Delta\omega_G^2]$ .

zian with a center at frequency  $\omega_L$  and a halfwidth  $\Delta\omega_L$  we obtain

$$\frac{\omega_s}{\Gamma_p} = \frac{\omega_0 - \omega_L}{\Delta\omega_L}$$

For a Gaussian excitation contour, the result of numerical integration of Eq. (6.10) is given in Fig. 22. Based on the results which have been presented one can conclude that it is completely realistic for  $\omega_s$  and  $\Gamma_p$  to be of the same order.

Let us now summarize the basic features of the phenomenon of the transition of alignment into orientation due to the dynamic Stark effect:

a) It is clearly a nonlinear effect, since its observed manifestation, the generation of circularly polarized fluorescence, depends cubically on the intensity of excitation; see Eq. (6.9);

b) the effect is of a quantum nature, since it disappears in the transition to a classical limit of large angular momenta;

c) it is manifested only in the presence of an external magnetic field, as is clear from Eq. (6.8).

In the case  $J \gg 1$ , a simplified system of equations for the motion of polarization moments can be used for a number of problems. The simplification consists of the switch to a classical limit  $J \rightarrow \infty$  in the coefficients of addition of angular momenta in Eqs. (6.2)–(6.4). As a result of an asymptotic transition we obtain<sup>40,156</sup>

$$L_1 A_{1\pm}^{L_2 L_3} = L_1 A_{\pm}^{L_2 L_3} = 0, \quad C_{\pm} = 1, \quad (6.11)$$

$$L_1 F_{L_1 L_2 L_3} = L_1 F_{\pm}^{L_2 L_3} = L_1 A_{\pm}^{L_2 L_3} = L_1 A_{1\pm}^{L_2 L_3} = L_1 S^{L_2 L_3} \\ = (-1)^{\Delta} \frac{\Pi_{L_2 L_3}}{\Pi_{L_1}} C_{1\Delta 1, -\Delta}^{L_2 L_3} C_{L_2 L_3 0}^{L_1}$$

where  $\Delta = J' - J''$ , and the system of equations (Eq. 6.1) is simplified

$$i\dot{\rho}_Q^K = \Gamma_p \sum_{X, X'} {}^K S^{X X'} \{ \Phi^{(X)} \otimes \alpha \rho^{(X')} \}_Q^K \\ - \Gamma_p \sum_{X, K'} {}^K S^{X K'} \{ \Phi^{(X)} \otimes \beta \rho^{(K')} \}_Q^K - (\Gamma_K - iQ\omega_J) \rho_Q^K, \quad (6.12a)$$

$$i\dot{\rho}_Q^{*K} = -\Gamma_p \sum_{X, X'} {}^* S^{X X'} \{ \Phi^{(X)} \otimes \alpha \rho^{(X')} \}_Q^{*K} \\ + \Gamma_p \sum_{X, K} {}^* S^{X K} \{ \Phi^{(X)} \otimes \beta \rho^{(K)} \}_Q^{*K} \\ - (\gamma_K - iQ\omega_J) \rho_Q^{*K} + \Gamma_{J', J''} \delta_{K X} \delta_{Q \beta} \rho_Q^K + \lambda_q^* \delta_{K 0} \delta_{Q 0}. \quad (6.12b)$$

The same classical polarization moments occur here as in Eq. (3.7). In the system of equations in Eq. (6.12) the terms which were proportional to  $\omega_s$  disappeared. The equations make it possible<sup>161</sup> to construct graphic images of the distribution of moments shown in Figs. 4, 5, 8, 10, 13, and 16.

A question arises here: What values of the quantum numbers  $J'$  and  $J''$  of the angular momentum are large enough for the asymptotic equations in Eq. (6.12) to be used? The answer depends to a significant degree on the type of molecular transition being examined, P, Q, or R. An estimate of the quality of the asymptotic approximation can be made by comparing the calculated values of the observed signal, for example, the degree of polarization of radiation, using accurate and asymptotic equations. Estimates show<sup>11,33,88</sup> that to obtain a calculation accuracy which is comparable with the accuracy which can be obtained from an experiment ( $\Delta P \sim 10^{-3}$ ) one can go over to the classical limit  $J \rightarrow \infty$ , for RP, PR, and QQ transitions, at  $J \sim 20$ , and for PP and RR transitions, only at  $J \sim 100$ . For a more specific answer to the question of the possibility of using asymptotic equations one must analyze each situation separately.

In conclusion it should be stressed that the system of equations in Eq. (6.1), and for  $J \gg 1$ , its asymptotic limit (Eq. (6.12)), apparently include all the basic effects which one should consider in approximations which are valid for broad-band excitation. The equations make it possible to describe the signals for the intensity and polarization of fluorescence which were examined in the previous sections, as well as their kinetics, the interference phenomena of level intersection signals, quantum beats, and parametric resonances, and also, signals recorded using polarization spectroscopy methods.

## 7. OTHER METHODS

The material presented to this point was based on the creation of an anisotropic distribution of angular momenta directly from the absorption of laser light. At the same time it is known, and in some cases has been known for a long time, that there are other means of aligning or orienting the angular momentum of diatomic molecules. Some of them, such as fluorescent population of high levels, or selective with respect to  $M''$  photodissociation, have much in common with the methods which have been presented. Polarization of the angular momentum resulting from collisions with other particles in gases or with a surface, as well as through the effect of an external inhomogeneous magnetic or electric field proceeds on a basis that differs in principle. However, even here there is much in common with optical pumping. The polarization characteristics of fluorescence stimulated by a laser is frequently used as an indicator of the anisotropy of angular momenta  $J$  which has been created. To describe the distribution of  $J$  one uses the multipole moments or coefficients which are proportional to them. Below we will examine, although rather briefly, some of the ideas and applications of various approaches to the creation of polarized molecules, including those which are not associated with light effects.

### 7.1. Fluorescent repopulation of levels

Along with optical "depopulation" of levels in molecules and atoms, Fig. 1, one can also perform optical pumping by "repopulation" of levels (Happer's terminology<sup>7</sup>)

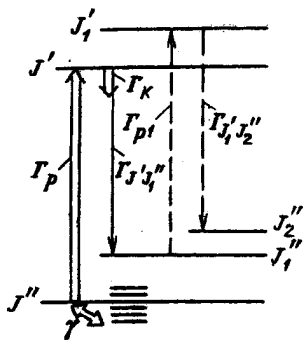


FIG. 23. Schematic for the creation and recording of optical pumping "repopulation."

through fluorescence in the cycle  $J'' \rightarrow J' \rightarrow J_1'$  (Fig. 23). Here, of special interest is the creation of orientation and alignment in thermally unpopulated high levels  $v_1', J_1'$  of the ground state. In the spontaneous process  $J' \rightarrow J_1'$  the polarization moments which are created in the process are transferred to level  $J_1'$  from the upper level  $J'$ . Thus, the state  $v_1', J_1'$  is optically aligned or oriented with a lifetime  $\tau_1 = \gamma_x^{-1}$ , and determines the rate of relaxation of the corresponding polarization moment  ${}_1\varphi_x^0$ .

From what has been said it is understood that in a certain sense this type of process virtually always takes place through a resonant series of fluorescence with the probability of the corresponding radiative processes. In this sense the process is sometimes called<sup>208</sup> "Franck—Condon pumping." The problem here is, first, creating a sufficient concentration of fluorescently repopulated states  $n_{J_1'}$ , and second, providing for their detection. The latter can be implemented with a second cycle of fluorescence,  $J_1' \rightarrow J_1' \rightarrow J_2''$  (see Fig. 23), which is stimulated by a probe beam  $\Gamma_{p1}$  of another frequency. This is one of the experimental methods in the spectroscopy of the modulation of population density, "marking the lower level," which was proposed by Kaminsky, Schawlow, *et al.*; see Refs. 77, 96, 163.

One can estimate what portion of the molecules are "pumped" to level  $v_1', J_1'$  from the ratio of constants  $k_{J_1'} = n_0 \Gamma_p \Gamma_{J_1' J_1'} / 3 \Gamma_1 \gamma$ , where  $\Gamma_1$  and  $\gamma$  are the relaxation constants of the upper and lower levels. An example of the calculation<sup>164</sup> is given in Fig. 24a for potassium dimers  $K_2$  in potassium vapor for parameters close to those given in Table III. It is clear that an increase in the vapor temperature, and therefore of the concentration of  $K_2$ , increases  $n_{J_1'}$  only to a certain limit, since the role of quenching collisions  $K_2(B^1\pi_u) + K$  increases.<sup>64</sup> An increase in the pumping power  $\Gamma_p$  also has a limit due to the increase in the nonlinearity of the process<sup>165</sup>  $\chi = \Gamma_p / \gamma$  in the depopulation of the lower level; see the curve in Fig. 24b.

Numerical modeling of the expected Hanle signals and quantum beats in optical pumping by "repopulation" is presented in Ref. 164. For weak pumping,  $\Gamma_p / \gamma \ll 1$ , one obtains rather simple expressions which describe the expected Hanle signal. For example, if the probe beam  $E_{p1}$  in the cycle  $J_1' \rightarrow J_1' \rightarrow J_2''$  is polarized orthogonally to the vector  $E_p$  in the cycle  $J'' \rightarrow J'$  (see Fig. 23), for the Q $\uparrow$  transition the degree of linear polarization on the scale of  $\omega_{J_1'} / \gamma \sim 1$  is

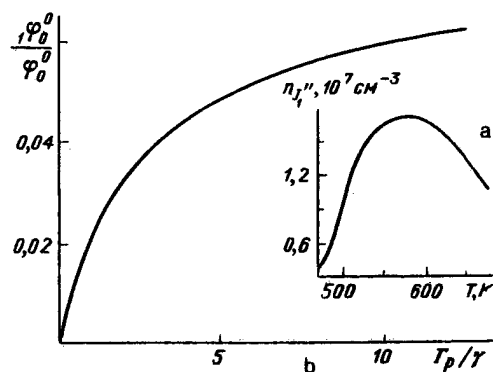


FIG. 24. a. Population density  $n_{J_1'}$  of high lying levels of  $K_2$  in the process of laser-induced fluorescence. b. The effect of optical depopulation. (Ref. 164).

$$Q^P(E_{p1} \perp E_p) = \frac{-4(\omega_{J_1'} / \gamma)^2}{1 + 8(\omega_{J_1'} / \gamma)^2}, \quad (7.1)$$

where  $\omega_{J_1'}$  is the frequency of precession of level  $J_1'$ . It follows from Eq. (7.1) that the signal has a large amplitude equal to 1/2.

Thus, the discussed means of pumping by "repopulation" to solve the problems of recording makes it possible to include it in the examination of high vibration-rotation levels. Their magnetism may exhibit a very interesting nature due to the closeness of the dissociation limit; see, for example, calculations for HF, DF, and TF in Ref. 166. The implementation of such experiments in the near future can be predicted.

## 7.2. Photodissociation and photoionization

The process of photodissociation occurs when molecules are excited to a certain state with subsequent spontaneous decay into the constituent atoms. Since the probability of photodissociation, in accordance with the material presented in section 2.3, depends on the angle between the  $E$  vector of the initiating light and the dipole moment of the transition  $d$ , the remaining intact molecules may be polarized to some extent. This type of experiment was first proposed in Ref. 167, and was later implemented<sup>168-170</sup> in the "pre-laser" era by Dehmelt *et al.* in a very simple molecular object, the  $H_2^+$  ion. When the authors introduced the term "selective photodissociation," they had in mind the selectivity of the process in terms of the directions of the angular momentum. The alignment effect of  $H_2^+$  in the ground state with rotation numbers  $< 2$  was detected through the magnetic resonance method between the Zeeman sublevels of the hyperfine structure in a magnetic field of  $50 \cdot 10^{-3}$  to  $115 \cdot 10^{-3}$  Gauss. The change in the number of ions retained in radio-frequency traps was recorded (Dehmelt received the Nobel Prize for physics in 1989 for his research). The experiments yielded information on the Landé factors and the hyperfine interaction constants of  $H_2^+$ .

The idea and theoretical description of the implementation of alignment of neutral molecules can be found in the works of Bersohn and Lin,<sup>171</sup> Zare,<sup>172</sup> and Ling and Wilson.<sup>173</sup> It follows from a classical examination that the distribution of the moments of molecules which remain intact

after, for example, the action of a linearly polarized laser pulse, depends on the type of transition: For a perpendicular transition (see Fig. 3c), the distribution is more isotropic than for a parallel transition (see Fig. 3b). A successful experiment of this type was performed by de Vries, Martin, *et al.*<sup>174</sup> IBr molecules which remained intact in a beam in the course of dissociation by the linearly polarized radiation from a Nd-YAG laser were found to be optically aligned. Since fluorescence occurs in a parallel P,R-type transition (see Fig. 3b), positive alignment of the angular momentum is created similar to Fig. 4a, and the plane of predominant rotation of the molecule is orthogonal to the light vector  $E$ . The proof consisted of the observed dependence of the chemoluminescence of the excimer molecules  $Xe^*I$  or  $Xe^*Br$ , which are the products of the reaction of IBr with an orthogonal atomic beam of metastable  $Xe^*$  angle between  $E$  and the relative velocities of the reagents. The results make it possible to draw a conclusion which is important for the understanding of the mechanism of forming an excimer, and that conclusion is that the cross section of the reaction is maximal if  $Xe^*$  is incident parallel to the plane of molecular rotation.

In a number of other experiments, not molecules, but atomic products were detected. Ling and Wilson<sup>173</sup> analyzed the angular distribution of the products of photodecay of a beam of IBr molecules, in particular,  $Br(^2P_{3/2,1/2})$  atoms, and confirmed the theoretical prediction. The works of Vasyutinskiĭ<sup>175,176</sup> for CsI and TlBr molecules showed that the conservation of angular momentum in the process of photodissociation using circularly polarized light leads to an orientation of the atoms which are formed. This orientation is manifested in the magnetic resonance of atomic products. This is true if the lifetime of the molecules in the unstable state in which photodissociation occurs is much smaller than the time that the electron moment of the molecule is coupled with its rotation, and the orientation created in the excited state is transmitted to atoms virtually without loss.

Developing the idea proposed in 1968 by van Brant and Zare,<sup>177</sup> a number of authors (see, in particular, Refs. 5, 178, and 179) studied the polarization of the fluorescence of atoms excited in the process of photodissociation of diatomic molecules. Ref. 179 presents a quantum mechanical calculation of the polarization properties of the fluorescence of photo-fragments. The results of experiments on  $Ca_2$  confirmed the need to consider the coherent effects which arise in quantum interference of the amplitudes of decay into various magnetic sublevels of the fragments, on the basis that the measured value of polarization of the  $^1P-^1S$  transition of Ca, which is equal to 0.64, was found to be closer to 0.78, which was obtained with a consideration of the coherence, than it was to the classical calculation, which yields 0.14.

In the process of photoionization one can also expect a partial alignment of the ions which are formed, and the degree of this alignment should be completely determined by the relative probability of alternative channels of ionization. One indicator of this alignment is the polarization of the fluorescence of a molecular ion. This experiment was successfully conducted with the ion  $N_2^+$  by Poliakoff, Zare, *et al.*<sup>180</sup> The process of photoionization of molecules of nitrogen  $N_2(X^1\Sigma_g^+) \rightarrow N_2^+(B^2\Sigma_u^+) + e^-(E_{\sigma_g}, E_{\pi_g})$  can occur in parallel ( $\sigma_g$ ) and perpendicular ( $\pi_g$ ) transitions. It follows from Eq. (3.14) and Table II that for photoionization in channel  $\sigma_g$ , when both dipole moments are in the plane of

rotation of the molecule and are independent,  $\langle \xi \rangle_\sigma = 45^\circ$ , the degree of polarization  $P = 1/7$ . For ionization in a  $\pi_g$  transition in the case of  $P\downarrow$ ,  $R\downarrow$  de-excitation  $\langle \xi \rangle_{\pi R} = \langle \xi \rangle_{\pi P} = 45^\circ$ , and for  $Q\downarrow$   $\langle \xi \rangle_{\pi Q} = 90^\circ$ , which on average yields  $P = -1/13$ . Thus, the observed polarization of ion radiation is

$$P_{\pi R} = (1-r)(7+13r)^{-1}, \quad (7.2)$$

where  $r = D_\pi^2/D_\sigma^2$  is the ratio of the strengths of the corresponding channels of photoionization; that is,  $P_{\pi R}$  depends only on  $r$ . The authors of Ref. 180 used ionization by synchrotron radiation  $\lambda = 450-660 \text{ \AA}$ , which corresponded to a photon energy from 18.75 eV (threshold) + 0.7 eV to about 27 eV. The measured values of  $P_{\pi R}$  were measured from, respectively, 0.052 to a value about a factor of two lower. The ratio  $D_\pi^2/D_\sigma^2$  was from 0.4 to 0.7.

### 7.3. Collisions of oriented particles

Here we begin an examination of the means of creating anisotropy in a system of angular momenta of the ground state of molecules which are not connected with the direct effect of light on the molecule. Let us examine the situation when the gas is a mixture of molecular and atomic components and conditions are specially created so that one can efficiently orient atoms optically. Then from the conservation of spin in molecular-atomic reactions one should expect that the molecular component will also be polarized.

Let us first examine the traditional system for optical pumping (in the way that Kastler used the term) of atoms: an optically oriented alkali atom  $A$  in a buffer medium of inert gas  $B$ . In alkali atoms, due to hyperfine interaction, the spins of the nuclei are also oriented. However, in this medium there is always an admixture of alkali dimers  $A_2$  in a diamagnetic  $^1\Sigma$  state. There are two basic collision mechanisms which lead to the transfer of orientation from atom  $A$  to dimer  $A_2$ : a) the creation and destruction of molecules in three-body collisions  $A + A + B \rightleftharpoons A_2 + B$ ; b) the atom-dimer exchange reaction  $A + A_2 \rightleftharpoons A_2 + A$ .

The dependence of the constants of dissociation  $k_D$  and recombination  $k_R$  in reaction (a) on the optical polarization of atoms  $A$  was predicted by Bernheim<sup>181</sup> and Kastler,<sup>182</sup> and was later demonstrated in Refs. 183 and 184. The dependence is linked with the obvious fact that only atoms with opposite electron spins can recombine into the molecule  $A_2(X^1\Sigma_g^+)$ , thus,  $k_R = k_R^0(1-S^2)$ , where  $S$  is the degree of electron spin polarization of the atoms. A very convenient indicator of the generation of dimers is the kinetics of laser-induced molecular fluorescence after magnetic resonance is introduced. This disrupts the polarization of the atoms; see the work of Huber and Weber<sup>185</sup> for a Na-Na<sub>2</sub> mixture.

A series of investigations<sup>186-192</sup> was carried out for the same mixtures but using the method of "optical pumping of molecules through atom-dimer exchange," which is associated with the detection of the signal of nuclear magnetic resonance of the dimers. The orientation of their nuclei is created in reactions (a) and (b) with the involvement of optically oriented atoms. A change in the orientation of the nuclear spins of dimers, in turn, through reverse reactions of decay and exchange, leads to a change in the orientation of alkali atoms  $A$ , and this is detected by a change in transmission of the resonant pumping light. The complexity of this



mechanism is compensated by the simplicity of the experiment, which is, in essence, a standard experiment for the optical orientation of atoms.<sup>6-10</sup> The width of the nuclear magnetic resonance signal is used to determine the constants of reactions (a) and (b) for Cs<sub>2</sub> and Rb<sub>2</sub> (Refs. 186 and 187), Na<sub>2</sub> (Ref. 188), and K<sub>2</sub> (Ref. 189). The values of the magnetic moments of the nuclei in alkali dimers were measured with great accuracy in Refs. 190 and 191. This made it possible to determine the difference of the constants of magnetic screening  $\sigma(A) - \sigma(A_2)$  between atoms and dimers (chemical shift) which, in turn, made it possible to estimate the constants of the spin-rotational hyperfine interaction  $c$ . It follows that  $H_{IJ} = chIJ$ , where  $c = 3g_I B_0 [\sigma(A) - \sigma(A_2)]$ ,  $g_I$  is the nuclear  $g$  factor, and  $B_0$  is the rotation constant. We note that more accurate values of  $c$  were obtained for <sup>23</sup>Na<sub>2</sub> (Ref. 100) and I<sub>2</sub> (Ref. 206) using the resonance method (see Table IV). The results for K<sub>2</sub>, Rb<sub>2</sub>, and Cs<sub>2</sub> from Ref. 191, despite the substantial errors, are the only ones available at this time.

Definitive grounds to presume the generation of polarized molecules is provided by recent results of Kartoshkin and Klement'ev<sup>192,193</sup> from studies of the conservation of the projection of spin (Wigner's rule) in spin exchange reactions and chemoionization in the collisions of spin-polarized metastable atoms of helium He\*(<sup>2</sup>S<sub>1</sub>) and neon Ne\*(<sup>3</sup>P<sub>2</sub>) with paramagnetic molecules O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and NO(<sup>2</sup>Π<sub>1/2</sub>). Spin-polarized products also result from the reaction of chemoionization in the collision of He with diamagnetic molecules, for example, with hydrogen<sup>194</sup> H<sub>2</sub> when H<sub>2</sub><sup>+</sup> ions are created in certain channels. However, in this and similar situations only atomic magnetic resonance signals were detected in the absence of direct experimental data on the polarization of molecular products.

#### 7.4. Alignment and orientation in beams

When a beam of molecules experiences scattering by other particles, for example, atoms, alignment of angular momenta (Fig. 25) may arise "downstream" in the beam. The collision mechanism to obtain a "polarized" beam of diatomic molecules was proposed in 1938 by Gorter.<sup>195</sup> The manifestation of alignment in a very simple model is associated with the anisotropy of the intermolecular potential in collisions. As a result, the scattering cross section of the molecule depends on the orientation of its angular momentum  $J$  with respect to the relative velocity  $v$ , of the colliding partners, which has its greatest value when its  $J \parallel v$ . If one considers, for example, the discharge of a stream of Na/Na<sub>2</sub> (Ref. 196) then both processes examined in section 7.3, a and b, act together, forcing the plane of rotation of the molecules to align in the direction of the flow, that is, "with the

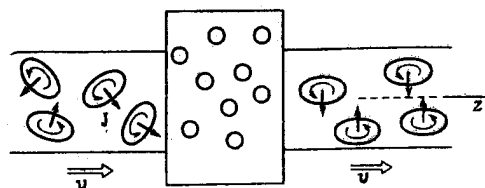


FIG. 25. Alignment of a molecular beam colliding with spherical symmetrical particles.

current" relative to the spherically symmetrical atoms. It can be said that a negative alignment of angular momenta of the ground state  $J$  is created which is similar to the one presented in Fig. 5b, where the axis of symmetry of the distribution is the direction of the flow  $z$ . It follows from the statements in section 4 that one of the methods of detecting the effect is to decrease the degree of polarization of fluorescence  $P$  if  $I_{\parallel}$  in Eq. (3.14) means polarization along the beam, and  $I_{\perp}$  means polarization along the laser beam used for excitation. The value  $P$  depends on the the first three even multipole moments of orders 0, 2, and 4, which characterize the alignment. This means of detection was proposed and implemented by Sinha, Zare, *et al.*<sup>196</sup> using  $B^1\Pi_u - X^1\Sigma_g^+$  fluorescence of type Q1Q1 in Na<sub>2</sub> excited by a Ar<sup>+</sup> laser (488.0 nm). A decrease in  $P$  was observed from 0.48 to 0.44 with an increase in pressure in the oven. It is important to note that here the laser beam does not create a nonlinear alignment of the ground state, it is only used to indicate it; that is, it should be a probe beam. This increase in the effect with an increase in pressure confirms its "collisional" nature. It can be easily seen from Eqs. (4.5) and (4.6) and Fig. 6 that in alignment due to nonlinear absorption,  $P$  increases as pressure increases, while the parameter  $\chi = \Gamma_p / \gamma$  decreases due to an increase in  $\gamma$ .

Direct confirmation of the alignment created in the beam is its precession in the magnetic field, which was observed in the changes in fluorescence in the work of Visser *et al.*,<sup>197</sup> and recently, in the work<sup>208</sup> of Pullman and Herschbach on I<sub>2</sub>. The authors of Ref. 208 normalized to comparable conditions and summarized the results of previous studies on Na<sub>2</sub> (Refs. 182, 196, 197), Li<sub>2</sub> (Ref. 207), and I<sub>2</sub> (Ref. 208) in a supersonic stream of an inert gas. One can conclude that the fortunate choice of a similarity factor (the product of the pressure of saturated vapors of the source by the diameter of the nozzle) makes it possible to obtain a substantial degree of alignment (up to  $\rho_0^2 / \rho_0^0$  from  $-0.3$  to  $-0.4$ ). In our opinion, the term "auto-alignment in beams" is suitable for this type of alignment mechanism. This term was introduced by Chalka in Ref. 198, which analyzed how auto-alignment caused features of the Hanle signal for a beam of NO<sub>2</sub>, which were unexpected by the authors of Ref. 199.

Another source of alignment in the beam is the process of beam formation itself, for example, in the nozzle in the discharge of a supersonic stream. This process was studied in Refs. 196 and 197 and is also determined by the product of the pressure by the diameter of the nozzle (scaling law).

Recently there have been rather intensive studies of the generation of alignment and orientation in collisions with a crystal surface; see, for example, Refs. 131 and 200, where Sitz, Kummel, and Zare measured even order multipole moments  $\kappa = 2$  and 4 (longitudinal alignment) and odd order multipole moments  $\kappa = 1$  and 3 (orientation), which arise in nitrogen molecules in the scattering of a supersonic beam of N<sub>2</sub> by a pure silver crystal Ag (111). The anisotropy of the angular momenta was detected using an extremely sensitive method of resonantly enhanced multi-photon ionization REMPI. Using the simplest time-of-flight equipment, the ions which were formed were selected by mass and recorded in an ion collection chamber with an almost 100 percent efficiency in the absence of a background. The problem of extracting information on the anisotropy of angular mo-

menta from the data of  $m + n$  REMPI was examined in Refs. 202, 203 and other publications. The authors used a two-photon resonance and a four-photon ionization ( $2 + 4$  REMPI) with rotation of the plane of polarization or a change in the ellipticity of the laser radiation used for excitation. A high degree of negative alignment was found of the angular momenta of  $N_2$  with  $J = 14$  relative to the normal to the surface due to the anisotropy of the acting forces. Of special interest is the detection of the orientation (chirality), which indicates the presence of "surface friction" type effects. Results on the generation of alignment of rotational states as the result of inelastic scattering of NO molecules by a Pt(111) crystal can be found in Ref. 201.

In addition to the collision mechanisms examined above which create an anisotropy of angular momenta, the historically earliest methods are also used. These methods use the effect of external magnetic and electric fields. This refers in particular to the famous Stern-Gerlach method from the dawn of quantum mechanics. The method makes it possible to "filter out" a beam with defined magnetic moment directions. The possibilities of the method were expanded by using magnetic resonance, including magnetic resonance in molecules. Magnetic moments were determined in the investigations of Ramsey, and the constants of hyperfine interaction for  $H_2$  and alkali dimers were determined from the shape of the resonance line (see Refs. 27, 132 and Table IV). A summary of the data on other molecules can be found in Ref. 35. Drawbacks of the method are the complexity of the set-up, insufficient sensitivity, and the lack of selection of vibration-rotation states; thus, the basic direction of research has been associated with replacing the magnet with optical (laser) means of polarizing molecules; see the examples in section 5.

A widely used method is the orientation of molecules in beams using an external focusing electric field with a special (hexapole) configuration; see Ref. 204 concerning the idea and principles of the method.

Unfortunately, even large, virtually unattainable values of the electric field lead only to insignificant orientation in diatomic molecules. On the other hand the method has been quite successfully applied to polar molecules of the symmetrical top type, and it has been especially successful with methylhalogens,  $CH_3F$ , ...,  $CH_3I$ , chloroform  $CHCl_3$  and similar molecules, and recently, with a larger class of polyatomic molecules. For details see Ref. 209 and the references therein.

### 8. CONCLUSION

This review basically contains an examination of the methods of creating and detecting the polarization of the angular momenta of simple molecules. It also deals with the coherence and interference of magnetic sublevels in these systems. The main, most obvious, and advancing field requiring the creation of polarized molecules is the study of the role of spatial orientation of particles and their angular momenta in inelastic collisions, in "semicollisions" in the process of photodissociation, and especially in collisions which lead to a chemical reaction. Oriented beams of reagents make it possible in direct experiments to reveal the effect of the spatial ("steric") factor on the probability of a reaction and on the angular distribution of products. The role of opti-

cal methods here is reduced to the production of polarized reagents with the selection of vibration and rotation levels and the testing of the polarization and angular distribution of reaction products. One of the first successful experiments of this type was presented in Ref. 205. To obtain information about the spatial dynamics of collisions one can use not only beams, but also the methods of laser optical orientation in bulk which were examined in this review. One can expect an expansion of studies related to the role of alignment and orientation in the interaction of a beam of molecules with a surface.<sup>131,200,201</sup> One indication of the appearance of a new branch of chemical dynamics devoted to the problems examined here is the first working conference on dynamic stereochemistry in November 1986 (Jerusalem), and a symposium of the Faraday Society on polarization effects in reactive collisions in December 1988 (West Germany). The materials from these meetings can be found in the publications containing Refs. 210 and 211. In the future, one could imagine some "ideal" stereodynamic experiment in which reagents are oriented in given states and records are made of the distribution over internal degrees of freedom, the angles of divergence, and of the orientation of products, and, when required, in real time.

Less popular is the use of the optical polarization of molecules and coherent effects for structural studies. Here, in our opinion, there are opportunities which have not been fully appreciated, primarily, opportunities to obtain information from the values of Landé factors. This information might be useful. Precise values of the Landé factors systematized according to vibration and rotation levels of the ground states and states excited by electrons could be obtained from experiments on the interference of coherent sublevels (intersection of levels, quantum beats, parametric resonances). Their values and signs are an extremely sensitive indicator of the various interactions occurring within the molecule<sup>29</sup> caused by the rotation of a diatomic molecule or a spin-orbit interaction. In the first case, for example, the Landé factor of the  $^1\Sigma$  state can be, in a number of cases, expressed directly in terms of the value of  $\lambda$  doubling of a distant  $^1\Pi$  term of appropriate symmetry which is interacting with it. The interaction between terms also has a noticeable effect on the  $g$  factor in paramagnetic states with large angular momenta ( $\approx 100$ ) whose magnetism is very small. A comparison of the measured Landé factors with theoretical calculations could provide a new viewpoint on a number of old problems associated with the study of perturbations within the molecule.

Finally, one should not forget that virtually every spectroscopist encounters a "nonspherical" distribution of the angular momenta of a molecular gas. If laser sources of excitation are used, nonlinear effects, in particular, optical polarization of the lower level, will be a common phenomenon, and it may turn out to be necessary to be able to evaluate it and take it into account.

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