

*RELAXATION IN THE SUBLEVEL SYSTEM OF THE EXCITED STATE OF  
ALKALI METAL ATOMS COLLIDING WITH NOBLE GAS ATOMS*

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A general expression is obtained which describes relaxation of the density matrix of excited atoms during collision with noble gas atoms. It is assumed that reorientation of the nuclear moment does not occur during the collision. The relative values of the decay constants for the orientation, alignment, and octupole moment of the electron shell for a state with angular momentum  $\frac{3}{2}$  ( $\gamma_1:\gamma_2:\gamma_3 = 0.92:1.14:1.01$ ) are determined by numerical solution of the collision problem and under the assumption of Van der Waals interaction between the atoms. The Van der Waals constants are estimated in order to determine the absolute values of the decay constants. The relaxation matrix in the system of hfs sublevels is expressed in terms of  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$ .

## INTRODUCTION

TRANSITIONS between sublevels of the excited (P) state of alkali metals in collisions with noble-gas atoms have been under intense investigations in recent years. Information concerning these collisions are obtained by experiments on the Hanle effect, on the intersection of levels, etc. (see [1-2]). In addition, collision mixing in the excited state leads to a characteristic dependence of the optical-pumping signal on the pressure of the buffer gas, and particularly to a reversal of the sign of the signal with increasing pressure. [4-7]

The determination of the cross sections from the experimental data requires, however, a detailed theory of collision relaxation in the excited state. The point is that the excited state of an alkali atom has a large number of degenerate or almost degenerate (hfs) sublevels. The reduction of the experimental data calls for the knowledge of the relations between the cross sections for transitions between all these sublevels. In addition, in experiments of the type of the Hanle effect an important role is played by the relaxation of different non-diagonal elements of the density matrix (coherence relaxation).

In a number of papers devoted to the determination of the collision cross sections from the experimental data, they used various types of arbitrary assumptions regarding the relative values of the cross sections. It was proposed that all the cross sections are the same or that different selection rules hold for the corresponding transitions. [6, 8-10]

We develop in this paper a theory of collision relaxation of both the diagonal elements of the density matrix (populations) and of the non-diagonal elements (coherence).

The main assumption is that collision gives rise to a change of only the state of the electron shell, and the state of the nucleus does not have time to change. Such an approximation is justified, since the characteristic duration of the collision is shorter than the reciprocal hyperfine splitting of the levels of the atoms.

Collisional relaxation in the electron shell is fully described only by a small number of constants—the

relaxation times of the momenta of the density matrix. [11-17] For a state with an electron shell with momentum equal to  $\frac{3}{2}$ , there are three such constants.

To calculate these three constants we use a procedure developed in [13], which includes a numerical solution of the equations for the probability amplitudes. A Van der Waals interaction was assumed between the alkali and the noble atoms.

Allowance for the hyperfine structure does not require the introduction of additional constants, and can be easily effected by changing over to the F,  $m_F$  representation in the equations for the density matrix, [14, 18] using the rule of vector addition of the angular momenta.

As the result, we obtain an explicit form of the relaxation matrix describing the mixing inside the state  $^2P_{3/2}$ .

For the first excited state of cesium or rubidium, it is possible to neglect transitions from the state  $^2P_{3/2}$  to the state  $^2P_{1/2}$ , since the duration of the collision is larger than the reciprocal of the fine splitting of the term.

The results of the calculation are compared with experimental data.

## 1. RELAXATION IN ELECTRON SHELL

Let us consider the excited state of an alkali atom, characterized by an electron angular momentum J. Following the method of [13], the rate of change of the electronic part of the density matrix of this state, due to the collisions with the atoms of the noble gas, can be written in the form

$$\left(\frac{\partial f_{mm'}}{\partial t}\right)_{\text{collision}} = -n \int \Delta f_{mm'} \rho d\rho v^3 dv \Phi(v) d\Omega, \quad (1)$$

$$d\Omega = \sin \theta d\theta d\varphi d\psi.$$

Here n is the concentration of the noble-gas atoms,  $\theta$  and  $\varphi$  are the polar angles of the relative-velocity vector  $\mathbf{v}$ ,  $\rho$  is the impact parameter,  $\psi$  is the azimuthal angle of the vector  $\rho$  in a plane perpendicular to  $\mathbf{v}$ ,  $\Phi(v)$  is the distribution of the relative velocities, normalized to unity (Maxwellian distribution with reduced mass). The symbols m and m' characterize the projections of the angular momentum of the electron shell on a certain selected quantization axis.

In formula (1),  $\Delta f_{mm}'$  is the change of the density matrix of the alkali atom after one collision

$$\Delta f_{mm}' = f_{mm}' - f_{mm}^A \quad (2)$$

where  $f_{mm}'$  is the density matrix prior to the collision and  $f_{mm}^A$  is the density matrix after the collision. Obviously, the matrix  $f_{mm}^A$  is expressed linearly in terms of  $f_{mm}'$ . It is convenient in practice to consider collisions in a coordinate system that is rigidly connected with the vectors  $\rho$  and  $\mathbf{v}$ .

The change over to the laboratory frame is effected in standard fashion with the aid of finite-rotation matrices. Calculations similar to those performed in [13] allow us to transform (1) into

$$\left( \frac{\partial f_q^{\kappa}}{\partial t} \right)_{\text{collision}} = -\gamma_{\kappa} f_q^{\kappa} \quad (3)$$

Here  $f_q^{\kappa}$  are the coefficients of expansion of the density matrix in the irreducible tensor operators. The quantity  $f_q^{\kappa}$  is proportional to the quantum-mechanical average component  $q$  of the moment of order  $\kappa$  of the electron shell of the atom. For example, the quantity  $f_0^0$  is proportional to the population of the state under consideration,  $f_q^1$  ( $q = 0, \pm 1$ ) are proportional to the mean values of the circular projections of the dipole (magnetic) moment, etc. Equations (3) thus describe the change of the mean values of the moments of different orders under the influence of the collisions. The quantities  $\gamma_{\kappa}$  are the reciprocal relaxation times of these moments.

Thus,  $\gamma_0$  is the constant of the decay of the total population of the excited state (in our case, obviously,  $\gamma_0 = 0$ );  $\gamma_1$  is the decay constant for the orientation of the excited state (for the dipole magnetic moment),  $\gamma_2$  is the decay constant for the alignment (for the quadrupole electric moment),  $\gamma_3$  is the decay constant for the octupole magnetic moment of the atom, etc. It is important that all the moments decay independently of each other and all the components of a moment of given order  $\kappa$  have identical decay constants. This is a consequence of the isotropy of the collisional relaxation.

The explicit form of  $\gamma_{\kappa}$  is given by the formula

$$\gamma_{\kappa} = (2J+1)(-1)^{\kappa+2J} \sum_j (-1)^j \left\{ \begin{matrix} J & J & j \\ J & J & \kappa \end{matrix} \right\} g_j, \quad (4)$$

$$g_j = 8\pi^2 n \int \Phi(v) v^3 dv \rho \cdot d\rho \left\{ \delta_{j,0} - \sum_n |M_{jn}|^2 \right\}, \quad (5)$$

$$M_{jn} = \left( \frac{2j+1}{2j-1} \right)^{1/2} \sum_{r,s} (-1)^{J-r} \left( \begin{matrix} J & J & j \\ r & -s & n \end{matrix} \right) P_{rs}. \quad (6)$$

The coefficient  $P_{rs}$  is the amplitude of the probability that the atom after the collision has an angular momentum projection  $r$ , under the condition that prior to the collision its angular momentum projection was  $s$  (in the coordinate system rigidly connected with the vectors  $\rho$  and  $\mathbf{v}$ ). In order to find these coefficients, it is necessary to choose the concrete form of the interaction of the colliding atoms and to solve the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} P_{mm'}(t) = \sum_{m_1} V_{mm_1} P_{m_1 m'}(t) \quad (7)$$

under the initial conditions

$$P_{mm'}(-\infty) = \delta_{mm'}. \quad (8)$$

Formula (6) contains the values of  $P_{mm'}(t)$  at  $t = +\infty$ .

## 2. SOLUTION OF THE COLLISION PROBLEM

For the interaction of the alkali atom in the excited state with the noble-gas atom, the first nonzero term in the expansion of  $V$  in the reciprocal powers of the distance between the atoms gives the Van der Waals interaction (dipole-dipole interaction in second order of perturbation theory):

$$V_{mm_1} = - \sum_{na} \frac{\langle m, 0 | U | a, n \rangle \langle n, a | U | 0, m_1 \rangle}{E_n + E_a - E_m - E_0}. \quad (9)$$

The symbol  $n$  pertains here to the states of the alkali atoms, and  $a$  to the states of the noble-gas atom, while the symbol zero corresponds to the ground state of the noble-gas atom.  $E$  is the energy of the corresponding states, with  $E_m$  in fact independent of the symbol  $m$ .

The dipole-dipole interaction  $U$  is given by

$$U = \frac{d\rho}{R^3} - 3 \frac{(d\rho)(pR)}{R^5}, \quad (10)$$

where  $R$  is the distance between the atoms and  $d$  and  $p$  are the dipole-moment operators of the alkali and noble atoms, respectively.

If we direct the quantization axis along the line joining the atoms, then the matrix  $V_{mm_1}$  is diagonalized and its diagonal elements have the meaning of the contribution of the interaction between the atoms to the quasimolecule energy. The electrostatic interaction does not lift the degeneracy completely. The levels with angular momentum projections  $\pm \frac{3}{2}$  become degenerate, as well as levels with projections  $\pm \frac{1}{2}$ .

The corresponding values of the interaction energy are denoted by  $(-c_{3/2}/R^6)$  and  $(-c_{1/2}/R^6)$ .

With the aid of formulas (9) and (10) we obtain the following expression for the Van der Waals constants  $c_{3/2}$  and  $c_{1/2}$ :

$$c_m = \sum_{na} \frac{|\langle m, 0 | (d\rho - 3d_0 p_0) | a, n \rangle|^2}{E_n + E_a - E_m - E_0}; \quad (11)$$

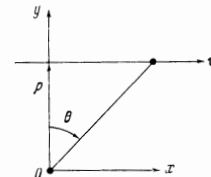
$d_0$  and  $p_0$  are the projections of the operators of the dipole moments on the quantization axis.

We direct the quantization axis along the line joining the atoms. This line rotates during the collision process. Since equations (7) have been written out for a coordinate system that is rigidly connected with the vectors  $\rho$  and  $\mathbf{v}$ , it is necessary to change over to this immobile coordinate system.

The matrix elements  $V_{mm_1}$  in any coordinate system can be expressed in terms of the constants  $c_{3/2}$  and  $c_{1/2}$ , since  $V_{mm_1}$  is transformed under rotations in accordance with the direct product of the representations  $D^{(J)*} \times D^{(J)}$  (we recall that in this case  $J = \frac{3}{2}$ )

$$V_{mm_1} = - \frac{1}{R^6} \sum_m D_{m'm}^{(J)*} D_{m'm_1}^{(J)} c_m. \quad (12)$$

The finite-rotation matrices  $D$ , the explicit form of



which is given in <sup>[19]</sup>, depend on the rotation angles.

We let the origin coincide with the alkali-metal atom. The  $x$  axis is directed along the velocity of the incoming noble-gas atom (the trajectory of the noble-gas atom is assumed to be a straight line<sup>1)</sup>). The  $y$  axis is directed along the vector  $\rho$ . In the chosen coordinate system (see the figure), the matrix elements  $V_{mm_1}$ , in accordance with formula (12), take the form

$$V_{\gamma/2, \gamma/2} = -\frac{1}{4R^6}(c_{\gamma/2} + 3c_{\gamma/2}), \quad V_{\gamma/2, \gamma/2} = -\frac{1}{4R^6}(3c_{\gamma/2} + c_{\gamma/2}),$$

$$V_{\gamma/2, -\gamma/2} = \frac{\sqrt{3}}{4R^6} e^{2i\theta}(c_{\gamma/2} - c_{\gamma/2}).$$
(13)

The remaining matrix elements satisfy the relations

$$V_{mm_1} = +V_{-m, -m_1}^* = V_{m_1 m}^*, \quad V_{m, m \pm 1} = 0. \quad (14)$$

The matrix elements determined by formulas (13) and (14) must be substituted in (7). We make in these equations the substitution

$$P_{mm'}(t) = u_{mm'}(t) \exp\left[\frac{i}{\hbar} \int_{-\infty}^t \frac{c_{\gamma/2} + c_{\gamma/2}}{2R^6} dt\right]. \quad (15)$$

In addition, we introduce as a variable the angle  $\theta$  (see the figure):

$$t = \frac{\rho}{v} \operatorname{tg} \theta, \quad R = \frac{\rho}{\cos \theta}. \quad (16)$$

Then Eq. (7) take the form

$$i \frac{d}{d\theta} u_{\gamma/2} = -z \cos^4 \theta \left( \frac{1}{\sqrt{3}} u_{\gamma/2} + e^{2i\theta} u_{-\gamma/2} \right), \quad (17)$$

$$i \frac{d}{d\theta} u_{-\gamma/2} = -z \cos^4 \theta \left( -\frac{1}{\sqrt{3}} u_{-\gamma/2} + e^{-2i\theta} u_{\gamma/2} \right);$$

$$i \frac{d}{d\theta} u_{-\gamma/2} = -z \cos^4 \theta \left( \frac{1}{\sqrt{3}} u_{-\gamma/2} + e^{-2i\theta} u_{\gamma/2} \right), \quad (18)$$

$$i \frac{d}{d\theta} u_{\gamma/2} = -z \cos^4 \theta \left( -\frac{1}{\sqrt{3}} u_{\gamma/2} + e^{2i\theta} u_{-\gamma/2} \right);$$

$$z = \frac{\sqrt{3}}{4} \frac{c_{\gamma/2} - c_{\gamma/2}}{v\rho^3 \hbar}. \quad (19)$$

In Eqs. (17) and (18), the second symbols of the functions  $u$  have been omitted, since they indicate only the initial conditions under which it is necessary to solve the system of equations

$$u_{mm'}(-\pi/2) = \delta_{mm'}. \quad (20)$$

We see that the system (7), in terms of the chosen coordinates, breaks up into two independent systems,

<sup>1)</sup>Neglect of the change of the atom velocity in a depolarizing collision can be justified by the following argument. The distance  $R$  between the atoms, at which a transition takes place between the sublevels of the excited state, is given in order of magnitude by the equation  $\hbar/V(R) = R/v$ . On the left we have the time of the transition and on the right we have the duration of the collision,  $V(R)$  is the interaction, and  $v$  is the relative velocity of the colliding atoms. The change of the atom velocity after covering such a distance is of the order of  $\Delta v \approx (R/Mv)\nabla V$ . Thus,

$$\frac{\Delta v}{v} = \frac{\hbar}{Mv} \frac{\nabla V(R)}{V(R)}$$

For a Van der Waals interaction at a temperature 300°K and  $R \sim 10^{-7}$  cm we have  $\Delta v/v \sim 10^{-1} - 10^{-2}$ , so that neglect of this quantity is justified.

so that no transitions with  $\Delta m = \pm 1$  take place. This does not mean at all, however, that some selection rules exist in the laboratory coordinate system.

In the calculation of  $\gamma_K$  in accordance with formulas (4)–(6), it is possible to substitute  $u_{\text{RS}}(+\pi/2)$  for  $P_{\text{RS}}$ , since the phase separated in the transformation (15) does not influence the result.

As seen from (17) and (18), the values of  $u_{\text{RS}}$ , and consequently also of  $M_{jn}$ , depend on  $v$  and  $\rho$  only via a single parameter  $z$  (the Massey parameter). Replacing the integration variable  $\rho$  in (5) by  $z$ , and integrating over the velocities, we obtain for the coefficients  $g_j$  the expression

$$g_j = \frac{n\bar{v}s}{2J} \int_0^\infty z^{-J/2} \left( \delta_{j0} - \sum_n |M_{jn}|^2 \right) dz, \quad (21)$$

where  $\bar{v} = (8kT/\pi\mu)^{1/2}$  is the average relative velocity of the alkali atom and of the noble-gas atom,  $\mu$  is the reduced mass of these atoms,  $J = \frac{3}{2}$  is the electron angular momentum, and

$$s = \frac{3(24\pi^4)^{1/2} \Gamma(2/5)}{5} \left( \frac{c_{\gamma/2} - c_{\gamma/2}}{\bar{v}\hbar} \right)^{2/5}. \quad (22)$$

Equations (17) and (18) subject to the initial conditions (20) were solved with a computer, and the integrals contained in (21) were evaluated. Table I lists the obtained values of the coefficients  $g_j$  and  $\gamma_K$ . We note that the sum of all the  $g_j$  is equal to zero; this follows also from (21), if it is recognized that

$$\sum_{jn} |M_{jn}|^2 = 1.$$

Table I gives only the relative values of the decay constants. We note that the calculation of these relative quantities does not involve any assumptions concerning the magnitude of the Van der Waals constants. However, to find the absolute values of the decay constants it is necessary to calculate the quantity  $s$ , and consequently to determine the Van der Waals constant.

### 3. CALCULATION OF $s$

We now proceed to calculate the Van der Waals constants entering in formula (22). Starting from (11) and taking into account the fact that the energies in the denominator do not depend on the magnetic quantum numbers, we obtain the expression

$$c_{\gamma/2} - c_{\gamma/2} = 3 \sum_{an} \frac{\{ |\langle 1/2 | d_0 | n \rangle|^2 - |\langle 3/2 | d_0 | n \rangle|^2 \} |\langle 0 | p_0 | a \rangle|^2}{E_n + E_n - E_m - E_0}. \quad (23)$$

The energy differences ( $E_n - E_m$ ) pertaining to the alkali atom are small compared with the resonant excitation energy of the noble gas. This makes it possible to carry out an expansion in powers of the ratio  $(E_n - E_m)/(E_a - E_0)$ . The coefficient of the first power of this small ratio turns out to be equal to zero, by virtue of the theorem concerning the sum of the oscillator

Table I

$\kappa$	$g_{\kappa} n \bar{v} s$	$\gamma_{\kappa} n \bar{v} s$
0	0.97	0
1	-0.21	0.92
2	-0.44	1.14
3	-0.32	1.01

strengths. The next term of the expansion (quadratic) can be estimated with the aid of the virial theorem for the alkali metal and the functions calculated in [20] for the noble gases. An estimate has shown that the contribution of this term does not exceed several per cent. Thus, in formula (23) we can retain only the zeroth term of the expansion and write it in the form

$$c_{1/2} - c_{3/2} = \{ \langle 1/2 | d_0^2 | 1/2 \rangle - \langle 3/2 | d_0^2 | 3/2 \rangle \} 3 \sum_{\alpha} \frac{|\langle 0 | p_0 | \alpha \rangle|^2}{E_{\alpha} - E_0}, \quad (24)$$

or

$$c_{1/2} - c_{3/2} = \frac{2}{3} e^2 \langle r^2 \rangle < \alpha. \quad (25)$$

Here  $\alpha$  is the polarizability of the noble gas,  $\langle r^2 \rangle$  is the mean square of the distance of the valence electron from the nucleus for the alkali atom in the excited state under consideration, and  $e$  is the electron charge.

The quantity  $\langle r^2 \rangle$  was calculated by means of the formula for the p-state of the hydrogen atom, in which the principal quantum number was taken with allowance for the quantum defect. Thus, the following values were obtained:  $\langle r^2 \rangle = 38, 49, 55,$  and  $63$  for the first-excited states of Na, K, Rb, and Cs, respectively. The values of  $\langle r^2 \rangle$  are given in units of  $a_0^2$  ( $a_0$ —Bohr radius). For comparison we indicate that the calculations of Bauer and Callaway, [21] using wave functions calculated by the self-consistent-field method, led to values 40.1 and 52.0 for Na and K, respectively.

Table II lists the values of  $s$  calculated using formulas (22) and (25). With the aid of  $s$  and Table I it is possible to obtain the absolute values of the decay constants of the orientation, alignment, and octupole moment of the electron shell of the alkali atom in the excited state due to collisions with noble-gas atoms.

The results make it possible to obtain the total relaxation matrix for the state  $^2P_{3/2}$  of the alkali atoms with allowance for the hyperfine structure.

#### 4. RELAXATION OF THE DENSITY MATRIX WITH ALLOWANCE FOR THE HYPERFINE STRUCTURE

In the presence of nuclear spin, the density matrix of the atom depends not only on the quantum numbers characterizing the electron shell, but also on the nuclear spin projections. It is convenient to introduce the quantity  $f_{qQ}^{\kappa K}$ , which has the meaning of the average product of the momentum of the electron shell of order  $\kappa$  on the momentum of the nucleus of order  $K$ . [18] The connection between this quantity and the density matrix in the  $m, M$  representation  $\chi_{mM, m'M'}$  ( $m$  is the projection of the momentum of the electron shell,  $M$  is the projection of the momentum of the nucleus) is given by

$$\chi_{mM, m'M'} = \sum_{\kappa=0}^{2J} \sum_{K=0}^{2I} \sum_{q=-\kappa}^{\kappa} \sum_{Q=-K}^K (\hat{T}_{-q}^{\kappa})_{mm'} (\hat{T}_{-Q}^K)_{MM'} (-1)^{q+Q} f_{qQ}^{\kappa K}, \quad (26)$$

where  $I$  is the spin of the nucleus,  $J$  is the angular mo-

mentum of the electron shell,  $\hat{T}_Q^K$  is the irreducible tensor operator customarily employed in the analysis of isotropic relaxation of the density matrix (see, e.g. [13, 14]). The inverse relation can be obtained with the aid of the orthogonality properties of the tensor operators.

Since the duration of the collision is much shorter than the reciprocal hyperfine splitting, the state of the nucleus does not have time to change during the collision. Therefore the equation characterizing the relaxation of  $f_{qQ}^{\kappa K}$  will have the same form as Eq. (3), namely

$$\left( \frac{\partial f_{qQ}^{\kappa K}}{\partial t} \right)_{\text{collision}} = -\gamma_{\kappa} f_{qQ}^{\kappa K}. \quad (27)$$

The decay constant  $\gamma_{\kappa}$  characterizes the decay of the momentum  $\kappa$  of the electron shell and does not depend on  $K$ . Using (26) and the inverse transformation, and changing over to the  $F, m_F$  representation with the aid of the vector-addition formulas, we obtain the following relation describing the relaxation of the density matrix  $\rho_{Fm_F, F'm'_F}$  in the collisions

$$\left( \frac{\partial \rho_{Fm_F, F'm'_F}}{\partial t} \right)_{\text{collision}} = - \sum_{F_1, m_1} \Gamma_{F_1, m_1}^{F, m_F, F_1, m_1} \rho_{F_1, m_1, F_1, m_1}, \quad (28)$$

where the relaxation matrix  $\Gamma$  is given by

$$\Gamma_{F_1, m_1}^{F, m_F, F_1, m_1} = \sum_{j_n} [(2F+1)(2F'+1)(2F_1+1)(2F_1+1)]^{1/2} (-1)^{m'-m} \times \begin{pmatrix} F & F_1 & j \\ -m & m_1 & n \end{pmatrix} \begin{pmatrix} F' & F_1' & j \\ -m' & m_1' & n \end{pmatrix} \left\{ \begin{matrix} J & j & J \\ F_1 & I & F \end{matrix} \right\} \left\{ \begin{matrix} J & j & J \\ F_1' & I & F' \end{matrix} \right\} (2J+1) g_j. \quad (29)$$

In formulas (28) and (29),  $F$  and  $m$  characterize respectively the total angular momentum of the atom and its projection. The quantities  $g_j$  are connected with  $\gamma_{\kappa}$  by the relation (4). Formula (29) is general and describes the relaxation inside the state with an electron-shell momentum  $J$  via the constants  $g_j$ . The nuclear spin enters only in the  $6j$ -symbols. Since the sum  $g_j$  is zero, the relaxation is described completely by  $2J$  independent constants. As applied to the first-excited states of Rb and Cs, these constants were calculated in the preceding sections.

From the properties of the  $3j$  symbols that enter in formula (29) it follows that the collisions connect only those elements of the density matrices  $\rho_{Fm, F'm'}$  and  $\rho_{F_1, m_1, F_1, m_1'}$ , for which  $m - m' = m_1 - m_1'$ . In addition, it follows from the properties of the  $6j$ -symbols that  $j \leq 3$ , and therefore only the relaxation-matrix elements for which  $|m_1 - m| \leq 3$  differ from zero. This "selection rule" is a direct consequence of the assumption that the projection of the angular momentum of the nucleus on the quantization axis does not change upon collision. As to the other selection rules discussed in the literature (e.g.,  $\Delta m = 0 \pm 2$ , and  $m_1 \neq -m$ ), they do not exist. This is seen, for example, from Table III, which gives the probabilities of the transitions between the Zeeman sublevels in the simplest case  $I = 0$ . The negative numbers in Table III characterize the total probability of departure from a given level because of collisions.

It is possible to introduce the cross section  $\sigma_{Fm, F'm}$  characterizing the departure from a given level,  $F, m$  in the collisions:

$$\sigma_{Fm} = \frac{1}{n\bar{v}} \Gamma_{Fm, Fm}^{Fm, Fm}. \quad (30)$$

Table II. Values of  $s$   
 $\times 10^{16}$  ( $\text{cm}^2$ ) at  
 $T = 300^\circ\text{K}$

	He	Ne	Ar	Kr	Xe
Rb	57	93	193	250	315
Cs	60	106	209	273	348

**Table III.** Relative probabilities of the transitions  
 $(-\Gamma_{Jm_1, Jm_1}^{Jm_1, Jm_1}/n\bar{v}s$  between the Zeeman sublevels  
 $\Gamma_{Jm, Jm}$  for  $I = 0$  and  $J = \frac{3}{2}$

m	m <sub>1</sub>				m	m <sub>1</sub>			
	3/2	1/2	-1/2	-3/2		3/2	1/2	-1/2	-3/2
3/2	-0.75	+0.30	+0.27	+0.18	-1/2	+0.27	+0.22	-0.79	+0.30
1/2	+0.30	-0.79	+0.22	+0.27	-3/2	+0.18	+0.27	+0.30	-0.75

This cross section can be expressed in terms of the quantities  $s$  listed in Table II:

$$\sigma_{Fm} = k_{Fm}s, \quad k_{Fm} = k_{F, -m}. \quad (31)$$

By way of an example, we give the values of the coefficients  $k_{Fm}$  for  $^{87}\text{Rb}$  ( $I = \frac{3}{2}$ ):

$$k_{3,3} = 0.74; \quad k_{3,2} = 0.90; \quad k_{3,1} = 0.91; \quad k_{3,0} = 0.91; \quad k_{2,2} = 0.90; \\ k_{2,1} = 0.92; \quad k_{2,0} = 0.97; \quad k_{1,1} = 0.94; \quad k_{1,0} = 0.91; \quad k_{0,0} = 0.97.$$

For  $^{85}\text{Rb}$ , these quantities lie in the range  $0.74 \leq k_{Fm} \leq 0.97$ . We note that all the  $k_{Fm}$  are of the order of unity. Therefore the values of  $s$  given in Table II characterize correctly the order of magnitude of the collision cross sections.

## 5. APPLICATIONS OF THE RESULTS

Let us see how the developed theory can be used to calculate quantities measured in concrete experiments.

1. Level intersection. In the case of an isolated intersection of the two levels of the excited state, importance attaches only to the density-matrix non-diagonal element that relates the intersecting levels. The collision broadening of the intersection signal is determined by the decay constant of this matrix element. We can obtain for this constant the following expression:

$$\gamma_{fm, f'm'} = (2J+1)(-1)^{m-m'} \sum_j g_j \eta_{fm}^j \eta_{f'm'}^j, \quad (32)$$

where

$$\eta_{fm}^j = \sum_{F, F'} \text{Re}(c_{fm}^{F, F'}) [(2F+1)(2F'+1)]^{1/2} \begin{pmatrix} F & F_1 & j \\ -m & m & 0 \end{pmatrix} \begin{Bmatrix} J & j & J \\ F_1 & I & F \end{Bmatrix} \quad (33)$$

In formulas (32) and (33), the indices  $f$  and  $f'$  denote the total angular momenta, which characterize the intersecting levels in the absence of a magnetic field, and  $m$  and  $m'$  are the projections of these momenta.

The quantities  $c_{fm}^F$  are the expansion coefficients of the eigenfunctions  $\Psi_{fm}^F(H)$  of the Hamiltonian in the magnetic field  $H$  in terms of the functions  $\psi_{Fm}$  in a zero field:

$$\Psi_{fm}^F(H) = \sum_F c_{fm}^F(H) \psi_{Fm}. \quad (34)$$

In practice it is possible to insert in (33) the values of the coefficients  $c_{fm}^F$  for the field  $H$  corresponding to the intersection. The formulas (32) and (33) were derived using (29) and (34), by converting the density matrix into a representation that diagonalizes the Hamiltonian in the magnetic field. Thus, to take into account the influence of the collisions on the width of the intersection signal, it is necessary to add to the natural width of the level the quantity  $\gamma_{fm, f'm'}$  determined by formula (32).

2. The Hanle effect (intersection of levels in a zero field). In this case an important role is played by the elements of the density matrix  $\rho_{F, m; F, m+\kappa}$  which are diagonal in  $F$  but are not diagonal in  $m$  ( $\kappa = 1$  for orientation). Elements with different values of  $\kappa$  do not get entangled by the relaxation matrix (29). This matrix, however, connects elements with different  $F$  and  $m$ . Thus, to calculate the signal with allowance for collisions it is necessary to solve the system of equations for  $\rho_{F, m; F, m+\kappa}$  at fixed  $\kappa$ . The number of levels can be decreased with the aid of a procedure used by Omont.<sup>[14]</sup> It is important that the influence of the collisions on the Hanle effect in the presence of the hyperfine structure cannot be characterized by a single cross section.

3. Optical orientation. In the case of pumping by circularly-polarized light, the principal role is played by diagonal elements of the density matrix  $\rho_{Fm, Fm}$  (populations).

To take into account the mixing in the excited state, it is necessary to add to the usual balance equations the relaxation term (28), in which only the diagonal elements of the density matrix are retained.

Unfortunately, the presently available experimental data are insufficient for a detailed comparison with the proposed theory. The most direct information on the values of  $g_j$ , which enter in the theory could be obtained, in our opinion, from experiments on the level intersection. However, in the papers known to us, no data are given on the dependence of the widths of the individual intersection signals on the noble-gas pressure. Gallagher<sup>[2]</sup> and Chaika and co-workers<sup>[1]</sup> give cross section values determined from the broadening of the Hanle-effect line, for collisions of Rb and Cs in the  $^2P_{3/2}$  state with certain noble gases. These cross sections do not differ strongly from the values of  $s$  given in Table II. A direct comparison, however, is impossible, because, as already noted above, the influence of the collisions on the Hanle effect cannot be characterized in general by a single cross section.

In<sup>[6,7]</sup> are given the values of the pressures  $P_0$  if the inert gas, at which the Cs and Rb optical-orientation signals go through zero in the case of pumping by the  $D_2$  line. The balance equation in optical pumping does not depend on the buffer gas. Its concentration and specific features enter only in the parameter  $n\bar{v}s$ . Therefore  $P_0\bar{v}s/kT$  should have the same value for all the noble gases for a given alkali atom. Table IV gives the values of this quantity, calculated using the experimental values of  $P_0$  and the values of  $s$  from Table II. The indicated property is satisfied within the limits of experimental error for all noble gases except helium. The measurement errors are much smaller for the ratios of  $P_0$  of the two Rb isotopes. It follows from Table IV that these ratios are independent of the type of the inert gas, with a high degree of accuracy. An

**Table IV.** Values of  
 $(P_0\bar{v}s/kT) \times 10^{-8} \text{ (sec}^{-1}\text{)}$

	He	Ne	Ar	Kr	Xe
$^{87}\text{Rb}$	0.36	0.63	0.74	0.58	0.69
$^{85}\text{Rb}$	0.24	0.51	0.62	0.48	0.57
$^{138}\text{Cs}$	0.36	0.68	0.65	0.55	0.58

exception is again helium. Probably, for helium the Van der Waals interaction is not predominant, owing to the small polarizability. We indicated in this connection the work by Faroux and Brossel,<sup>[22]</sup> who investigated the depolarization of mercury in the  $6^3P_1$  state in collisions with noble gases as a function of the temperature. They observed that for Ar, Kr, and Xe the interaction is of the Van der Waals type, whereas for He and Ne a shorter-range interaction predominates.

We emphasize in conclusion once more that in our theory no account is taken of transitions between fine-structure levels. This is justified if the fine splitting exceeds the reciprocal collision time. For lithium, and also for higher excited states of other alkali atoms, the relation is reversed. In these case it can be assumed that the projection of the electron spin (as well as the projection of the nuclear spin) remains unchanged in the collisions. The matter reduces only to reorientation of the orbital angular momentum. Formulas (4)–(6) remain in force also when  $J$  is replaced by  $L$ . We note that the values of  $\gamma_K$  for  $L = 1$  in the case of a Van der Waals interaction were calculated by Rebane.<sup>[16]</sup> The changeover to the relaxation matrix in  $F, m_F$  representation can be carried out in accordance with the rule for the vector addition of the angular momenta.

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