

Kinetics of decay of metastable gas phase of polarized atomic hydrogen at low temperatures

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The stability of the polarized gas phase of atomic hydrogen in a strong magnetic field and at low temperature is investigated. The cross section for nonresonant threshold depolarization due to exchange and dipole-dipole interaction in pair collisions is found. It is shown that dipole-dipole interaction is predominant in strong magnetic fields. Below-barrier resonance recombination into highly excited hydrogen molecule states located at a distance of less than $2\mu_B H$ from the boundary of the continuous spectrum is considered. It is noted that this decay channel can be suppressed at the expense of the centrifugal barrier. Nonthreshold decay channels involving three-particle recombination with a change of the spin state are studied in detail. The probabilities of these processes are found for exchange and dipole-dipole interaction, remain finite as $T \rightarrow 0$, and impose thereby a restriction on the attainable density of the polarized gaseous phase. The role of surface effects is considered. It is shown that surface recombination can be overcome and in low temperatures corresponding to Bose condensation can be attained, in principle, only if the atoms accumulate in a state with parallel electron and nuclear spins.

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1. INTRODUCTION

The problem of metastable states of matter that result from polarization of the electron spins of atoms in a system has been attracting great interest of late. The system most intensively discussed is polarized atomic hydrogen, in which spin alignment prevents the recombination of the atoms into a molecule and leads to the appearance of a quasistable atomic phase. In the case of hydrogen one can speak even at the very lowest temperatures of a gas and of a condensed system.

A direct solution of the problem of the pair collision of two hydrogen atoms in the triplet state leads to a scattering length $a_t = 0.72 \text{ \AA} > 0$ (see Sec. 2). This result corresponds to an increase of the energy E of the rarefied polarized gas with increase of its density n , and by the same token to a stabilization of the gas phase. Whether this phase is stable or metastable depends on the behavior of the function $E(n)$ at high densities. As shown by numerical calculations,¹⁻³ the energy turns out to be a monotonic function of n , and consequently polarized atomic hydrogen by itself does not form a condensed phase and remains a gas at $T=0$. On the other hand, a polarized condensed phase should be a solution of atomic hydrogen in a foreign matrix. We note for comparison that in the case of tritium we have obtained $a_t < 0$, and consequently the condensed phase should be stable at $T=0$ in this case.

Of particular interest is the gas phase of atomic hydrogen, a phase readily seen to be a weakly interacting Bose gas with relatively high Bose-condensation temperature T_0 even at limited densities.

The possibility of obtaining and using polarized atomic systems depends to a decisive degree on their lifetime, which is determined primarily by the spin depolarization process. In the gas phase, the depolarization takes place in collisions of atoms in a

volume, and also in collisions with a surface and with atoms adsorbed on it. The present paper is devoted to an investigation of the kinetics of the decay of the metastable-gas phase of polarized atomic hydrogen on account of volume depolarization and recombination with change of the spin state. The role of surface effects is discussed separately.

We are interested in temperatures of the order of several degrees or lower, and also in strong polarizing magnetic fields satisfying to the inequality

$$\xi = \mu_B H / T \gg 1. \quad (1.1)$$

When considering pair collisions, we immediately encounter two significant peculiarities. First, by virtue of the condition (1.1) the depolarization is essentially inelastic. Second, even at these temperatures the de Broglie wavelength of the hydrogen atom becomes comparable with the characteristic radius of the interatomic interaction, and this makes it necessary to treat the motion of the nuclei in the course of the collision quantum-mechanically. This distinguishes in principle our problem from the ordinary problems of the theory of atomic collisions.

The depolarization in collisions of polarized hydrogen atoms is due in principle to three types of interaction: exchange, spin dipole-dipole, and interaction of the spin with the orbital motion of the nuclei. It is known that even in extremely strong magnetic fields the presence of a hyperfine interaction causes hydrogen atoms with zero total-spin projection to be in a state that contains an admixture of a state with all opposite projection of the electron spin (see, e.g., Ref. 4). The scale of this admixture is determined by the ratio

$$\kappa = A / 4\mu_B H \ll 1, \quad (1.2)$$

where A is the hyperfine interaction constant. The collisions of the particles in such a "mixed" state with arbitrary other polarized atoms can lead to depolari-

zation on account of exchange interaction, as governed by the small parameter (1.2). In this paper we develop a quantum-mechanical theory of this depolarization process (see Sec. 2).

The presence of an exchange depolarization mechanism in pair collisions was actually first pointed out by Brown.⁵ To determine the probability of the depolarization, he modified the classical variant of the theory of resonant spin exchange (see, e.g., Ref. 6) to include the case when a magnetic field is present. Stwalley⁷ used later Brown's results⁵ to estimate the rate of depolarization of atomic hydrogen at low temperature in a strong magnetic field. This approach, however, is not appropriate for the considered problem at low temperatures, by virtue of the quantum character of the motion of the nuclei and of the strong inelasticity of the process, although the important statement that the rate of depolarization depends exponentially on the parameter (1.1) is undoubtedly correct.

At low temperatures, as it turns out, an essential role in the process of pair depolarization is played by dipole-dipole interaction. In this case depolarization results even if the weak hyperfine interaction is neglected. As will be demonstrated in this paper (see Sec. 3), in magnetic fields $H > 10^4$ Oe and at low temperature this depolarization mechanism is at any rate the dominant one among the pair processes.

The depolarization due to the spin-orbit interaction, as shown by our analysis (see Sec. 4), is practically always weak compared with the dipole-dipole depolarization.

In the case of pair collision, the depolarization process is always accompanied by an increase of the Zeeman energy by $2\mu_B H$. This predetermines its threshold character and accordingly a decrease of its rate with increasing parameter (1.1).

Besides depolarization, exchange interaction makes possible in pair collisions of polarized atoms the resonant process of recombination with transition of the quasimolecule into bound singlet states whose energy is located at a distance smaller than $2\mu_B H$ from the end point of the continuous spectrum. As shown by an analysis of the spectrum of the vibrational-rotational states of the H_2 molecule (see Sec. 5), this situation can be realized only for levels with a rotational quantum number $j \geq 10$, and the characteristic time of the resonant recombination turns out to be very long because of the high centrifugal barrier. The opposite seems to take place in deuterium or in a mixture of hydrogen and deuterium. Here resonant recombination into bound states with $j=0$ is possible, making this decay channel really dangerous (see Ref. 7).

Under conditions of strong increase in density, when multiparticle interactions become significant, we encounter the possible appearance of decay channels without thresholds (see Sec. 6). When considering the depolarization it is necessary to take into account the decrease of the energy of the produced particles with

flipped spin on account of the interaction with the background (see Ref. 8). This decrease of the energy $\Delta\epsilon$ increases with decreasing density, and if $|\Delta\epsilon|$ becomes larger than $2\mu_B H$, then the process of depolarization will have no threshold. Close to the usual density of the condensed state, the parameter $|\Delta\epsilon|$ is replaced by the width of the energy band of the spin waves. In this case the thresholdless decay of the polarized phase would take place without production of spin waves, with and without simultaneous emission of phonons.^{9,10}

The energy values of the collective excitations with spin flip in a Bose gas of polarized hydrogen atoms, given in Sec. 6, impose not too strong a restriction on the density at which the depolarization process still retains a threshold [the corresponding criterion differs radically from that obtained by Berlinsky,⁸ (see also Ref. 9), since Berlinsky assumed implicitly that particles with parallel and antiparallel spins have the same pair-correlation function]. It follows from the obtained criterion that the depolarization process retains its threshold in a wide range of densities, which certainly includes $n \sim 10^{21}$ cm⁻³.

At high densities an important role can be assumed by the process of simultaneous depolarization and recombination in ternary collision of polarized atoms. A pair of particles then forms a molecule in a bound excited state, and the excess energy is carried away by the third particle. An examination of such a peculiar recombination process, with allowance for the exchange and dipole-dipole interactions (see Secs. 7 and 8) shows that its rate remains finite as $T \rightarrow 0$. This imposes stringent restrictions on the gas density. For the exchange mechanism at $H = 10^5$ Oe, a decay time of the order of an hour corresponds to $n \sim 10^{17}$ cm⁻³ (this value increases with increasing H). For the dipole interaction the limitation is less stringent: $n \sim 10^{18}$ cm⁻³.

Even if we confine ourselves to such densities, however, we encounter the problem of the recombination that takes place on the surface, particularly with participation of the substrate atoms as the third body (see Sec. 9). In the region of the considered low temperatures, even relatively low adsorption energy is sufficient for a high surface density of the adsorbed atoms. This immediately turns on thresholdless depolarization processes, making even an ideally clean surface an effective "catalyst." Thus, the question of the surface with the minimum adsorption energy becomes fundamental. In this case coating with a helium film (adsorption energy less than 1 K) has no competition, accounting in fact for the success of the brilliant experiments of Silvera *et al.*^{11,12} as well as Clyne *et al.*¹³

As shown by our analysis, even in the case of a helium coating, exchange three-particle recombination on a surface with participation of a helium atom does not make it possible to obtain the indicated densities simultaneously with the infralow temperatures. However, if a spin-polarized atomic phase is prepared in a "clean" state with a nuclear spin polarized along

the electron spin, such a possibility remains in principle. The decisive factor here is the appearance of a surface-recombination channel with participation of the helium atom.

2. DEPOLARIZATION ON ACCOUNT OF EXCHANGE INTERACTION IN PAIR COLLISIONS

It is known that the system of spin wave functions of an isolated hydrogen atom in an external magnetic field can be written in the following form (see, e.g., Ref. 4):

$$\begin{aligned} \varphi_1 &= \alpha(+1/2)\beta(+1/2), \quad \varphi_2 = \alpha(+1/2)\beta(-1/2) + \kappa\alpha(-1/2)\beta(+1/2), \quad \varphi_3 = \alpha(-1/2)\beta(-1/2), \\ \varphi_4 &= \alpha(-1/2)\beta(+1/2) - \kappa\alpha(+1/2)\beta(-1/2). \end{aligned} \quad (2.1)$$

Here $\alpha(\sigma)$ and $\beta(m)$ are the spin wave functions of the electron and nucleus, respectively, while σ and m are the projections of the electron and nuclear spins on the magnetic-field direction. The states φ_2 and φ_4 have, even in a strong magnetic field, an admixture of a state with opposite projection of the electron spin. However, by virtue of the condition (1.2), the degree of their polarization is close to unity, and we shall refer to as polarized the two states φ_1 and φ_2 or φ_3 and φ_4 .

The Hamiltonian of the quasimolecule made up of two colliding atoms has in the c. m. s. the form

$$\hat{H} = -\hbar^2 M^{-1} \Delta_{\mathbf{R}} + U_1(R) + U_{ex}(R) + \hat{H}_z + \hat{H}_{hf}. \quad (2.2)$$

Here M is the mass of the atom, \mathbf{R} is the vector of the internuclear distance, $U_1(R)$ is the potential of the long-range interaction of the atoms,

$$U_{ex}(R) = \Delta(R) (\hat{S}_1 \hat{S}_2 + 1/4) \quad (2.3)$$

is the Hamiltonian of the exchange interaction ($\Delta(R) > 0$),

$$\hat{H}_z = 2\mu_B (\hat{S}_1 + \hat{S}_2) H$$

is the Hamiltonian of the Zeeman interaction, \hat{S}_1 and \hat{S}_2 are the operators of the electron spins of the atoms, and \hat{H}_{hf} is the Hamiltonian of the hyperfine interaction.

As $R \rightarrow \infty$ the spin states of the quasimolecule are determined by the Hamiltonian $\hat{H}_z + \hat{H}_{hf}$ corresponding to the eigenfunctions $\varphi_{i\hbar} = \varphi_i(1)\varphi_{\hbar}(2)$. Let the polarized phase of the atomic hydrogen be a mixture of atoms in states φ_3 and φ_4 (the magnetic moment of the electrons in these states is directed along the magnetic field). The exchange interaction (2.3) conserves the projection of the total (electron and nuclear) spin of the quasimolecule, and therefore does not lead to depolarization when two particles in the states φ_3 collide. However, if atoms in states φ_3 and φ_4 collide, then the interaction (2.3) can lead to the transition $\varphi_{24} \rightarrow (\varphi_{23} - \varphi_{32})/\sqrt{2}$. Such a transition corresponds to polarization of the electron spin of one of the atoms as they diverge to infinity. The magnetic element of the transition, taken with the spin variables, is equal to $\kappa\Delta(R)/\sqrt{2}$. The initial spin state corresponds to the triplet potential of the interaction of colliding atoms

$$U_1(R) = U_1(R) + \Delta(R)/2, \quad (2.4)$$

and the final state to the singlet potential

$$U_s(R) = U_1(R) - \Delta(R)/2. \quad (2.5)$$

In the final spin state, the total nuclear spin of the system is equal to unity [if we disregard the small addition to the wave function, proportional to the parameter $\kappa(1.2)$], i.e., we are dealing with an orthohydrogen quasimolecule, for which, as is well known, the rotational quantum number j in the singlet state can take on only odd values. Since the exchange interaction (2.3) does not depend on the angle variables, the angular momentum j does not change as a result of depolarization and consequently in the initial state j can likewise be only odd. Thus, in the case of the collisions $\{3, 4\}$ the depolarization takes place only at odd angular momenta j . Scattering with even j , on the contrary, is purely elastic.

When two atoms collide in the state φ_4 , the exchange-interaction operator (2.3) leads to transitions of the system from the initial spin state φ_{44} into a state with a wave function $(\varphi_{13} + \varphi_{31} - \varphi_{24} - \varphi_{42})/2$, corresponding to interaction of the atoms in accord with the singlet potential $U_s(R)$ (2.5). The matrix element of the transition, taken over the spin variables, is then $\kappa\Delta(R)$. Since the colliding atoms are identical, or since we are dealing in the final state with a parahydrogen quasimolecule (as is readily established from the form of the spin wave function), the angular momentum j can take on in this case only even values.

As seen from our analysis, the spin depolarization process is a nonresonant triplet-singlet transition. In the considered case, when the electron magnetic moments are polarized along the magnetic field, the kinetic energy of the atoms is decreased as a result of the depolarization by $2\mu_B H$. The fact that the transition from the state $\{4, 3\}$ takes place only into the state $\{3, 2\}$, and from $\{4, 4\}$ only into $\{4, 2\}$ and $\{3, 1\}$, is actually the consequence of the conservation of the projection of the total spin of the quasimolecule in the collision.

Bearing the condition (1.1) in mind, we determine now the depolarization cross section in first-order perturbation theory. Using the known expansion of the wave functions of nuclear motion in spherical harmonics (see, e.g., Ref. 14), we obtain

$$\sigma_{(34)} = \frac{\pi \kappa^2 M^2 R_0^6}{2\hbar^4} \frac{k_f}{k_i} \sum_{j=1}^{\infty} (2j+1) |L_j|^2, \quad (2.6)$$

$$L_j = \frac{1}{k_i k_f R_0^3} \int_0^{\infty} \chi_{jk_f}^{(*)}(R) \Delta(R) \chi_{jk_i}^{(i)}(R) dR. \quad (2.7)$$

The summation in (2.6) is only over odd j ;

$$k_i = i^{-1} (M\varepsilon_i)^{1/2}, \quad k_f = \hbar^{-1} (M\varepsilon_f)^{1/2}, \quad (2.8)$$

are the wave vectors of the relative motion of the atoms in the initial and final states of the quasimolecule, $\varepsilon_i > 2\mu_B H$ is the kinetic energy of the atoms colliding at infinity, and $\varepsilon_f = \varepsilon_i - 2\mu_B H$. The wave functions of the radial motion $\chi_{jk_f}^{(s)}(R)$ and $\chi_{jk_i}^{(i)}(R)$ are the solutions of the Schrödinger equations for the singlet (2.5) and triplet (2.4) potentials, respectively, and are normal-

ized by the condition

$$\int_0^{\infty} \chi_{jk}(R) \chi_{j'k'}(R) dR = 2\pi\delta(k-k'). \quad (2.9)$$

The distance $R_0 \approx 7a_0$ (a_0 is the Bohr radius) corresponds to the condition $U_t(R_0) = 0$ (see Fig. 1) and was introduced into Eqs. (2.6) and (2.7) for convenience. At low energies it corresponds to the characteristic interaction region that leads to depolarization.

The depolarization cross sections $\sigma_{\{44\}}$ are determined by the same relation (2.6), but with twice as large a numerical factor and with summation over only even j . Taking this into consideration, recognizing that there is no depolarization in the $\{3, 3\}$ collision, and assuming the same density of the atoms in the states φ_3 and φ_4 , we get for the average depolarization cross section

$$\sigma^{\text{ex}}(\varepsilon_i) = \frac{1}{8}(\sigma_{\{44\}} + 2\sigma_{\{34\}}) = \frac{\pi\kappa^2 M^2 R_0^6 k_f}{8\hbar^4 k_i} \sum_{j=0}^{\infty} (2j+1) |L_j|^2 \quad (2.10)$$

(the summation here is over all j).

At $R \geq R_0 \gg a_0$ the exchange interaction $\Delta(R)$ decreases exponentially with increasing R . Because of this circumstance, the main contribution to the depolarization cross section $\sigma^{\text{ex}}(\varepsilon_i)$ (2.10) is connected with the vicinity of the point R_0 .

Bearing in mind the problem at hand, we confine ourselves to an analysis of the depolarization cross section in the case of extremely low temperatures, on the order of 1 K and lower. By virtue of the threshold and of the conditions (1.1), in the case of spin flip the initial energy of the particles will be $\varepsilon_i \approx 2\mu_B H$ and the final energy $\varepsilon_f \lesssim T$. So low a final energy predetermines the leading role of s -scattering in the depolarization (at $\varepsilon_f \approx 1$ K the p -scattering becomes significant).

In the considered energy interval it is convenient to represent the wave functions $\chi_{0k_i}^{(t)}(k)$ and $\chi_{0k_f}^{(s)}(R)$ of the motion in the following form:

$$\chi_{0k_i}^{(t)}(R) = k_i \varphi_t(R, k_i), \quad \chi_{0k_f}^{(s)}(R) = k_f \varphi_s(R, k_f). \quad (2.11)$$

In the limit as $k_i, k_f \rightarrow 0$ the functions $\varphi_{s,t}$ cease to depend on the wave vector. Recognizing that $\varphi_t(r, 0)$

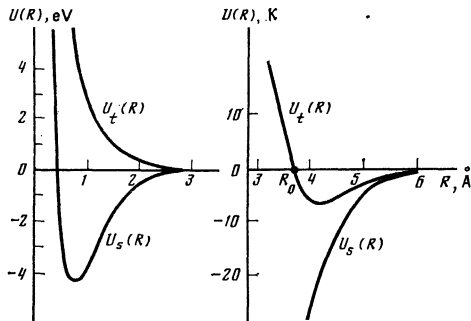


FIG. 1. Potential curves of the quasimolecule H_2 ; R is the internuclear distance, $U(R)$ is the potential energy of the interaction.

and $\varphi_s(R, 0)$ are solutions of the corresponding Schrödinger equations with $k=0$, we multiply the equation for the potential $U_t(R)$ by $\varphi_s(R, 0)$ and subtract from it the equation for the potential $U_s(R)$ multiplied by $\varphi_t(R, 0)$. As a result, we get for L_0 (2.7)

$$L_0 = \frac{\hbar^2}{MR_0^3} \int_0^{\infty} [\varphi_s(R, 0) \varphi_t''(R, 0) - \varphi_t(R, 0) \varphi_s''(R, 0)] dR = \frac{4\hbar^2}{MR_0^3} \frac{(a_t - a_s)}{R_0} (-1)^n, \quad (2.12)$$

where a_t and a_s are the scattering lengths in the triplet and singlet states and n is the number of discrete s levels in a singlet well.

In a strong magnetic field we must take into account primarily the dependence of the function φ_t on k_t . Thus, if the magnetic field is $H \sim 10^5$ Oe, then $\varepsilon_i \sim 13$ K and $k_t R_0 > 1$.

Substituting (2.11) in (2.7) and taking (2.12) into consideration, we obtain for the exchange-depolarization cross section in the case of s scattering

$$\sigma_0^{\text{ex}} = k_i^{-1} k_f \kappa^2 \sigma_0^{\text{ex}} g_0^2(\varepsilon_i, \varepsilon_f), \quad (2.13)$$

$$\sigma_0^{\text{ex}} = 2\pi (a_t - a_s)^2, \quad (2.14)$$

$$g_0(\varepsilon_i, \varepsilon_f) = \int_0^{\infty} \varphi_t(R, k_t) \Delta(R) \varphi_s(R, k_f) dR \int_0^{\infty} \varphi_t(R, 0) \Delta R \varphi_s(R, 0) dR. \quad (2.15)$$

To determine a_t , a_s , and $g_0(\varepsilon_i, f)$, we obtained the solutions of the Schrödinger equation for the triplet (2.4) and singlet (2.5) potentials (see Fig. 1) corresponding to the data of the variational calculation by Kolos and Wolniewicz.¹⁵ The results were $a_t = 0.72$ Å, $a_s = 0.33$ Å and consequently $\sigma_0^{\text{ex}} \approx 10^{-16}$ cm².

The obtained dependence of g_0^2 on ε_i for two values of the final energy, $\varepsilon_f = 0$ and $\varepsilon_f = 1$ K, is shown in Fig. 2a. In a magnetic field $H \approx 10^5$ Oe, the factor $\kappa^2 \approx 6 \cdot 10^{-6}$, $\varepsilon_i \approx 13$ K and if $\varepsilon_f \lesssim 1$ K we obtain for the exchange-depolarization cross section the estimate $\sigma_0^{\text{ex}} \approx 5 \cdot 10^{-24}$ cm².

Let us dwell briefly on the depolarization in scattering with $j=0$. At $\varepsilon_f \lesssim 1$ K the cross section for depolarization with $j \geq 2$ is much less than the cross section σ_0^{ex} . The reason is that even for $j=2$ the centrifugal potential at $R=R_0$ amounts to 21 K, and the effective potential in the singlet state acquires a barrier of height ~ 7 K at $R \approx 10a_0$. As for the cross section σ_1^{ex} , at $\varepsilon_f = 0$ it is naturally equal to zero.

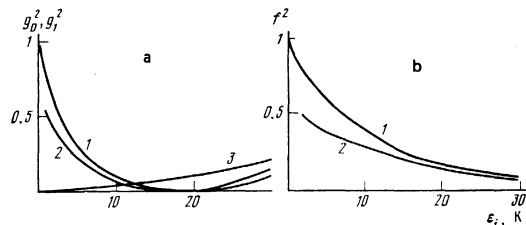


FIG. 2. Dependence of the factors g_0^2 and g_1^2 on the initial energy ε_i : curve 1) $g_0^2(\varepsilon_i)$ at $\varepsilon_f = 0$, curve 2) $g_0^2(\varepsilon_i)$ at $\varepsilon_f = 1$ K, curve 3) $-\varepsilon_f MR_0^2 g_1^2(\varepsilon_i) / \hbar^2$ at $\varepsilon_f = 1$ K. b) Dependence of the factor f^2 on the initial energy ε_i : curve 1) $f^2(\varepsilon_i)$ $\varepsilon_f = 0$, curve 2) $f^2(\varepsilon_i)$ at $\varepsilon_f = 1$ K.

With increasing ε_f , this cross section increases. At an energy as low as $\varepsilon_f \approx 1$ K it becomes relatively large in the region of those ε_f where the factor g_0^2 is small. The expression for σ_1^{ex} can be represented in the form

$$\sigma_1^{\text{ex}} = \frac{k_f}{k_i} \kappa^2 \sigma_{\text{ex}} \frac{\varepsilon_f M R_0^2}{\hbar^2} g_1^2(\varepsilon_f). \quad (2.16)$$

In the region of values $\varepsilon_f < 1$ K of interest to us, the dependence of the factor g_1 on ε_f is very weak.

Figure 2a shows a plot of the quantity $\varepsilon_f M R_0^2 g_1^2 / \hbar^2$ against ε_f at $\varepsilon_f = 1$ K. We note that $H \approx 10^5$ Oe the cross section σ_1^{ex} exceeds σ_0^{ex} by a factor of 2 (the cross section σ_2^{ex} is much smaller than $\sigma_0^{\text{ex}} + \sigma_1^{\text{ex}}$ in the entire considered interval of ε_f).

The characteristic time τ_{ex} of the bulk depolarization is determined by the rate constant of the process $\alpha_{\text{ex}} = \langle \sigma^{\text{ex}} v \rangle$ (v is the relative particle velocity, the angle brackets denote averaging over the Maxwellian distribution of the particles in the gas) from the relation

$$1/\tau_{\text{ex}} = \alpha_{\text{ex}} n, \quad (2.17)$$

where n is the density of the gas. Using the relations (2.13) and (2.16) for temperatures $T < 1$ K we have under the condition (1.1)

$$\alpha_{\text{ex}} \approx \kappa^2 \alpha_{\text{ex}} \left(\frac{H}{H_0} \right)^{1/2} \left[g_0^2(2\mu_B H, 0) + \frac{3TMR_0^2}{2\hbar^2} g_1^2(2\mu_B H, 0) \right] \exp\left(-\frac{2\mu_B H}{T}\right). \quad (2.18)$$

In this expression

$$\alpha_{\text{ex}} = \sigma_{\text{ex}} \frac{2\hbar}{MR_0} \approx 3.5 \cdot 10^{-12} \text{ cm}^3/\text{sec}, \\ H_0 = \hbar^2 / 2\mu_B M R_0^2 \approx 2.5 \cdot 10^6 \text{ Oe}.$$

The threshold character of the reaction leads to the appearance of the obvious small factor $\exp(-2\mu_B H/T)$. Therefore by a transition to infralow temperatures it is always possible, in principle, to attain an arbitrary decrease of the depolarization rate constant (cf. Ref. 7).

The dependence of the pre-exponential factor in (2.18) on the magnetic field at $T=0$ and $T=1$ K is shown in Fig. 3.

In concluding this section we shall trace the transformation of the obtained relations for the exchange-depolarization cross section on going to higher temperatures. If in place of the inequality (1.1) we have the inverse relation $\xi \ll 1$, then the depolarization process becomes quasi-elastic. In this case, when determining the overlap integral L_j (2.7), we can put approximately $k_i \approx k_f \approx k$. Then, following the same procedure as in the derivation of (2.12), we obtain

$$L_j = \frac{\hbar^2}{MR_0^2 k^2} \int_0^\infty [\chi_{jk}^{(s)}(R) \chi_{jk}^{(t)'}(R) - \chi_{jk}^{(t)}(R) \chi_{jk}^{(s)'}(R)] dR \\ = \frac{4\hbar^2}{MR_0^2} \frac{1}{kR_0} \sin[\delta_{sj}(k) - \delta_{tj}(k)].$$

Here δ_{sj} and δ_{tj} are the phases of the j -scattering in the singlet and triplet states. Substituting this expression in (2.10), we obtain for the depolarization

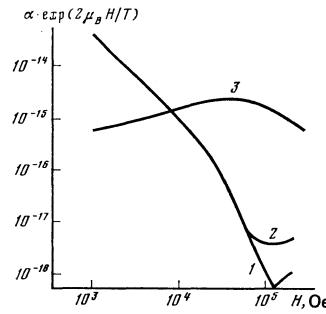


FIG. 3. Dependence of the pre-exponential factor in the formulas for the rate constants of the exchange (2.18) and the dipole-dipole (3.11) depolarization on the magnetic field. Curves 1 and 2 correspond to the exchange depolarization at $T=0$ and $T=1$ K. Curve 3 corresponds to dipole depolarization.

cross section

$$\sigma^{\text{ex}} = \frac{2\pi\kappa^2}{k^2} \sum_{j=0}^{\infty} (2j+1) \times \sin^2[\delta_{sj}(k) - \delta_{tj}(k)]. \quad (2.19)$$

In the high-energy region ($\varepsilon \gtrsim 300$ K), when the decisive contribution in (2.19) comes from collisions with large angular momenta j , we can determine the phase difference by using the quasiclassical approximation. In this case

$$\sigma^{\text{ex}} \approx 4\pi\kappa^2 \int_0^\infty \rho d\rho \sin^2 \left(\int_{-\infty}^\infty \frac{\Delta(\rho, t)}{2\hbar} dt \right) = 2\kappa^2 \sigma_{\text{res}}, \quad (2.20)$$

where ρ is the impact parameter of the collision, σ_{res} is the cross section for resonant spin exchange. The formula for σ_{res} is well known (see, e.g., Ref. 6). A result similar to (2.20) was obtained earlier by Brown.⁵

3. DIPOLE-DIPOLE POLARIZATION IN PAIR COLLISIONS

Spin depolarization in collision of two polarized hydrogen atoms can be due not only to exchange interaction but also to dipole-dipole interaction of the electron spins:

$$\hat{V}_d = \frac{4\mu_B^2}{R^3} \{ (\hat{S}_1 \hat{S}_2) R^2 - 3(\hat{S}_1 \cdot \mathbf{R})(\hat{S}_2 \cdot \mathbf{R}) \}. \quad (3.1)$$

The operator (3.1) does not change the total electron spin of the quasimolecule, but can change its projection M_s , on a preferred direction with $\Delta M_s = \pm 1, \pm 2$. This makes possible depolarization in collision of polarized atoms also when the hyperfine interaction is neglected. The depolarization corresponds then to a nonresonant triplet-triplet transition.

We obtain the depolarization cross section in first-order perturbation theory. Recognizing that in the triplet state, at a total quasimolecule nuclear spin $I=1$, the angular momentum assumes only even values, and at $I=0$ only odd values, we have for the cross section for depolarization with $\Delta M_s = 1$

$$\sigma^d(\varepsilon_i) = \frac{3\pi}{10} \left(\frac{\mu_B^2 M}{\hbar^2} \right)^2 \frac{k_f}{k_i} \left[3 \sum_{j_i=0}^{\infty} \sum_{j_f=0}^{\infty} J^2(j_i, j_f) (2j_i+1) (2j_f+1) \right. \\ \left. \times \begin{pmatrix} j_i & 2 & j_f \\ 0 & 0 & 0 \end{pmatrix}^2 + \sum_{j_i=1}^{\infty} \sum_{j_f=1}^{\infty} J^2(j_i, j_f) (2j_i+1) (2j_f+1) \begin{pmatrix} j_i & 2 & j_f \\ 0 & 0 & 0 \end{pmatrix}^2 \right] \quad (3.2)$$

(the symbols ' and '' correspond to summation over even and odd j). The overlap integral $J(j_i, j_f)$ is defined by the relation

$$J(j_i, j_f) = \frac{1}{k_i k_f} \int_0^{\infty} \chi_{j_i}^{(e)} \chi_{j_f}^{(e)} \frac{dR}{R^2}, \quad (3.3)$$

where the radial-motion wave functions $\chi_{j_k}^{(e)}(R)$ corresponding to the triplet potential are normalized by the condition (2.9); k_i and k_f are defined in accordance with (2.8).

From (3.2) there follows directly the selection rule $j_i - j_f = 0, \pm 2$ for the angular momentum of the quasimolecule. In addition, j_i and j_f cannot be simultaneously equal to zero.

We note that the cross section for the simultaneous spin flip of both atoms ($\Delta M_s = 2$) is determined by the same formula (3.2) but with twice as large a numerical factor and with

$$k_f = \hbar^{-1} [M(\varepsilon_i - 4\mu_B H)]^{1/2}, \quad \varepsilon_i > 4\mu_B H. \quad (3.4)$$

We determine first the cross section for dipole depolarization at the lower limit of the initial energy ε_i , corresponding to the condition $k_i R_0 \ll 1$ (weak magnetic field). In this case the overlap integral (3.3) is built up over the distances $R \sim 1/k_i \gg R_0$. We can then use for $\chi_{j_k}(R)$ the wave functions of the free motion:

$$\chi_{j_k}(R) = 2kR \mathcal{J}_j(kR), \quad (3.5)$$

where $\mathcal{J}_j(x)$ is a spherical Bessel function. In the case $j \neq 0$ this is obvious, but this can be done also at $j = 0$, recognizing that $\chi_{0k} \sim \sin k(R - a_j)$ and $ka_j \ll 1$.

Substituting (3.5) in (3.3) we obtain ($k_f < k_i$):

$$J(j_i, j_f) = \frac{\pi}{2} \left(\frac{k_f}{k_i}\right)^{1/2} \Gamma\left(\frac{j_i + j_f}{2}\right) F\left(\frac{j_i + j_f}{2}, \frac{j_i - j_f - 1}{2}, j_i + \frac{3}{2}, \left(\frac{k_f}{k_i}\right)^2\right) \times \left[\Gamma\left(j_i + \frac{3}{2}\right) \Gamma\left(\frac{j_i - j_f + 3}{2}\right)\right]^{-1}. \quad (3.6)$$

Here Γ is the gamma function and F is a hypergeometric function.

If $k_f \ll k_i$, then the leading transitions are $d \rightarrow s$. In this case we have $J(2, 0) = 4/3$. Substituting this result in (3.2), we get for the depolarization cross section

$$\sigma^d = \frac{k_f}{k_i} \sigma_s^d, \quad \sigma_s^d = \frac{8}{5} \pi R_0^2 \left(\frac{\mu_B^2 M}{\hbar^2 R_0}\right)^2. \quad (3.7)$$

In a strong magnetic field, a realistic situation is one in which

$$k_i R_0 \ll 1, \quad k_f R_0 \gg 1. \quad (3.8)$$

The $d \rightarrow s$ transitions are again decisive here. However, to calculate the overlap integral (3.3) we must now use the true wave functions, which are solutions of the Schrödinger equation for the real potential $U_+(R)$, since a substantial contribution to this integral under condition (3.8) is built up over distances comparable with R_0 . The overlap integral will decrease with increasing ε_i . Representing $J(2, 0)$ in the form $J(2, 0) = (4/3)f(\varepsilon_i, \varepsilon_f)$ we have correspondingly for the depolarization cross section at ΔM_s

$$\sigma^d = k_i k_f^{-1} \sigma_s^d f^2(\varepsilon_i, \varepsilon_f). \quad (3.9)$$

For the depolarization channel with $\Delta M_s = 2$ we obtain a similar expression with an additional factor 2 and under the condition that ε_i and ε_f are determined in accordance with (3.4). The dependence of f^2 on ε_i obtained as a result of direct calculations is shown in Fig. 2b, again for two values of the final energy, $\varepsilon_f = 0$ and $\varepsilon_f = 1$ K. The time τ_d of the decay of the polarized states of the atomic gas on account of the paired dipole polarization is determined by the relation (2.17), in which the rate constant is $\alpha_d = \langle \sigma^d v \rangle$. Using expression (3.9), we obtain for temperatures $T < 1$ K, with account taken of both depolarization channels,

$$\alpha_d \approx \alpha_d^* (H/H_0)^{1/2} \{ f^2(2\mu_B H, 0) \exp(-2\mu_B H/T) + 2f^2(4\mu_B H, 0) \exp(-4\mu_B H/T) \}. \quad (3.10)$$

Here $\alpha_d^* = \alpha_s^d \cdot 2\hbar / MR_0 \approx 3 \cdot 10^{-15}$ cm³/sec. Under the condition (1.1), the second term in (3.10) is small and α_d is determined in practice by the process with one spin flip. The contribution from transitions with all other combinations of j_i and j_f is also small compared with the obtained value of α_d .

The dependence of the pre-exponential factor in (3.10) on the magnetic field is shown in Fig. 3. As seen from the curves in this figure, at $H > 10^4$ Oe the dipole depolarization is decisive. If $H \approx 10^5$ Oe, then $\alpha_{ex} / \alpha_d \approx 2 \cdot 10^{-3}$. The reason for this result, which is unusual for magnetic relation processes, is the smallness which is characteristic of exchange polarization in the considered case.

We note that despite the small dipole-dipole interaction ($\mu_B^2 / R_0^3 \sim 10^{-2}$ K) and of the factor κ^2 , both rate constants α_{ex} (2.18) and α_d (3.10) turn out to be relatively large. This makes essential the use of the threshold factor $\exp(-2\mu_B H/T)$ to ensure a sufficiently long lifetime τ of the polarized state of the atomic gas. Thus, to obtain τ on the order of hours at a density $n = 10^{20}$ cm⁻³, the threshold factor must amount to $\sim 10^{-8} - 10^{-9}$. In a field $H \approx 10^5$ Oe this calls for temperatures $T \lesssim 0.6$ K.

4. ESTIMATE OF THE ROLE OF SPIN-ORBIT INTERACTION

Besides the exchange and the dipole-dipole interactions spin depolarization in collisions of polarized atoms can in principle be caused by the interaction of the electron spins with the orbital motion of the nuclei or, in other words, with the rotation of the quasimolecule axis. This interaction is, in particular, responsible for the rotation of the spin of the atom in a collision with an atom that does not have its own spin and orbital momenta.^{16,17}

It is easy to establish from general considerations that in collisions of hydrogen atoms the Hamiltonian of the spin-orbit interaction, averaged over the electron wave function, is of the form

$$\hat{V}_{so}(R) = \gamma(R) \hat{S} \hat{j}, \quad (4.1)$$

where \hat{j} is the operator of the total angular momentum

of the quasimolecule without allowance for the spin, and \hat{S} is the operator of the total electron spin. The expression for $\gamma(R)$ has the following structure:

$$\gamma(R) = \frac{\mu_B^2 m}{R^3 M} f(R), \quad (4.2)$$

where m is the electron mass. By virtue of the repulsive character of the triplet potential $U_t(R)$, the spin-orbit depolarization takes place over distances $R \gtrsim R_0$. Therefore the dimensionless quantity $f(R)$ turns out to be small compared with unity for all variants of the interaction, both those that do not take into account the distortion of the atomic wave functions, and those that do take this distortion into account; this distortion, in principle, can be substantial (see Refs. 16 and 17). It is clear, therefore, that the spin-orbit depolarization is weaker by many orders of magnitude than the dipole polarization considered in the preceding section.

5. RESONANT RECOMBINATION OF POLARIZED ATOMS IN STATES WITH LARGE j

As noted in the Introduction, bound states of a hydrogen molecule with large rotational quantum numbers can have energy values $E_{v,j}$ close to end point of the continuous spectrum. If at the same time

$$|E_{v,j}| < 2\mu_B H, \quad (5.1)$$

formation of a bound singlet state of the molecule becomes possible in pair collision of polarized atoms. This resonant process can be due only to exchange interaction, since dipole-dipole interaction does not lead to transitions from the triplet to the singlet state.

An analysis of the data on the spectrum of the vibrational-rotational states of the hydrogen molecule¹⁸ shows that the greatest trouble can be caused by the level $E_{12,10} \approx 10$ K. Other possible levels corresponding to the condition (5.1) could have only larger values of j and smaller values of v .

In transitions connected with exchange interaction, the rotational quantum number is conserved. By virtue of this, the states of the continuous spectrum are separated by a large centrifugal barrier from the bound states satisfying the inequality (5.1).

It is known that bound states with odd j are possessed only by molecules of orthohydrogen, and with even j only by parahydrogen molecules. Taking this into consideration, it is easy to verify that only ortho-hydrogen can be produced in collisions of atoms in states φ_3 and φ_4 [see (2.1)], and only para-hydrogen in collisions of two atoms in the state φ_4 .

We consider first the inverse process, namely the decay of a bound singlet state of a molecule. The matrix element of the transition from the exchange-interaction operator (2.3), taken over the spin variables, is equal to $2^{-(1/2)} \kappa \Delta(R)$ for the orthomolecule $\{3, 4\}$ transition. For the para molecule $\rightarrow \{4, 4\}$ transition it is equal to $\kappa \Delta R$. Bearing in mind that in the former case it is necessary to sum over two equivalent final states ($\{3, 4\}$ and $\{4, 3\}$), we obtain a single formula

for the probability of the decay of the bound state and an arbitrary value of j :

$$W_{vj} = \frac{\kappa^2 M}{\hbar^2 k_0} \left| \int_0^\infty \chi_{vj}(R) \Delta(R) \chi_{j k_0}^{(t)}(R) dR \right|^2. \quad (5.2)$$

Here $\chi_{vj}(R)$ is the radial wave function of the bound state, normalized to unity; $\chi_{j k_0}^{(t)}(R)$ is the radial wave function of the continuous spectrum for the triplet state, normalized by the condition (2.9);

$$k_0 = \hbar^{-1} (M(2\mu_B H - |E_{vj}|))^{1/2}. \quad (5.3)$$

Recognizing that the functions $\chi_{vj}(R)$ and $\chi_{j k_0}^{(t)}(R)$ are solutions of the Schrödinger equation for the singlet (2.5) and triplet (2.4) potentials, respectively, it is easy to show that

$$\int_0^\infty \chi_{vj}(R) \Delta(R) \chi_{j k_0}^{(t)}(R) dR = 2\mu_B H \int_0^\infty \chi_{vj}(R) \chi_{j k_0}^{(t)}(R) dR. \quad (5.4)$$

Substituting this result in (5.2) and using (1.2), we obtain

$$W_{vj} = A^2 M a_0^2 I_{vj}^2 / 4\hbar^2, \quad (5.5)$$

$$I_{vj} = k_0^{-1/2} a_0^{-1} \int_0^\infty \chi_{vj}(R) \chi_{j k_0}^{(t)}(R) dR. \quad (5.6)$$

Using now the detailed-balance principle, we can obtain the following expression for the rate constant of resonant recombination of polarized atoms:

$$\alpha_{vj} = \frac{1}{4} W_{vj} (2j+1) \left(\frac{4\pi \hbar^2}{MT} \right)^{3/2} \exp\left(-\frac{E_0}{T}\right), \quad (5.7)$$

$$E_0 = \frac{\hbar^2 k_0^2}{M}.$$

Let us estimate the value of the overlap integral I_{vj} (5.6). By virtue of the condition $j \gg 1$, which is predetermined by the inequality (5.1), we use the quasi-classical approximation for the function $\chi_{vj}(R)$. In the range of distances $R \gtrsim R^*$ (R^* is the position of the maximum of the effective single potential and depends little on the rotational quantum number), where the bulk of the integral I_{vj} is built up, the function $\chi_{j k_0}^{(t)}(R)$ practically coincides with the wave function of the free motion [$k_0 R^* \ll f$, $R_{t,j} < R^*$, where $R_{t,j}$ is the value of R at which the centrifugal potential coincides with $U_t(R)$]. Bearing in mind an upper-bound estimate, we assume for the definition of $\chi_{vj}(R)$ the limit $|E_{vj}| \rightarrow 0$, and for $\chi_{j k_0}^{(t)}(R)$ we retain the solution in the form (3.5) at $R > R^*$. Recognizing that at $R \gtrsim R^*$ the centrifugal potential greatly exceeds the singlet potential, we obtain after integrating in (5.6)

$$I_{vj} \approx \frac{C(j)}{j^{3/2}} \exp\left\{(j-1) \ln k_0 R^* - j \ln \frac{2j}{e}\right\}. \quad (5.8)$$

The factor $C(j)$, just as R^* , depends little on j . Its appearance is due to the presence of the normalizing factor in the singlet wave function, and to the fact that in a relatively narrow vicinity of the point $R_{s,j}$ ($U_{s,j}(R_{s,j}) = 0$) the centrifugal potential is comparable in magnitude with the singlet potential. Direct estimates at $j \sim 10$ show that $C(j) \sim 1$.

Substituting (5.8) in (5.5), we obtain the following

expression for the decay probability:

$$W_{vj} \approx \frac{A^2 M a_0^3 C^2(j)}{4\hbar^3 j} \exp\left\{ (j-1) \ln \frac{E_0}{E^*} - 2j \ln \frac{2j}{e} \right\}, \quad (5.9)$$

$$E^* = \hbar^2 / MR^2 \approx 4 \text{ K}.$$

We see from this that the decay probability and the rate constant (5.7) decrease rapidly with increasing rotational quantum number. The character of the function $\alpha_{vj}(E_0)$ is governed to a considerable degree by the relation between E_0 and T . This relation has a maximum at $E_0 = (j-1)T$. In this case

$$\alpha_{vj}^{\max} \approx \frac{0.2A^2 M a_0^3}{\hbar^3} \left(\frac{4\pi\hbar^2}{ME^*} \right)^{3/2} \left(\frac{T}{E^*} \right)^{j-1/2} C^2(j) \exp\left\{ -(j+1) \ln \frac{4j}{e} \right\}. \quad (5.10)$$

An estimate of expression (5.9) at the smallest possible $j=10$ yields

$$W_{vj} \approx 10^{-12} (E_0/E^*)^9 \text{ sec}^{-1}. \quad (5.11)$$

If $E_0 \approx 2\mu_B H$ and $H \sim 10^5$ Oe, then the lifetime $\tau_{vj} = W_{vj}^{-1} \sim 10^7$ sec. At all densities of interest, the molecule certainly experiences inelastic collisions during this time, and these collisions shift it to lower non-decaying states. The recombination rate is therefore actually determined by the constant α_{vj} (5.7), (5.10).

At $j=10$ we have

$$\alpha_{vj}^{\max} \approx 10^{-25} (T/E^*)^{1/2} \text{ cm}^3/\text{sec} \quad (5.12)$$

and in the temperature region $T < 3$ K it does not exceed $\sim 10^{-26}$ cm³/sec. This rate constant corresponds to a polarized-gas lifetime $\tau > 10^6$ with respect to the process of resonance recombination all the way to densities $n \sim 10^{20}$ cm⁻³. The polarized gas thus turns out to be stable with respect to this decay channel.

We emphasize, in concluding this section, that the stability of the polarized gas to resonant recombination is due decisively to the large value of the rotational quantum number of the corresponding discrete levels. If this is not the case and molecules can be produced in states with small j , then the considered decay channel may cause considerable trouble. Such a situation should apparently take place in deuterium or in a mixture of hydrogen with deuterium, a fact first pointed out by Stwalley.⁷

6. THRESHOLDLESS DEPolarIZATION. ROLE OF COLLECTIVE SPIN EXCITATIONS

We have seen that in pair collisions of polarized hydrogen atoms in a strong magnetic field the depolarization has in principle a threshold. This circumstance caused the appearance of the factor $\exp(-2\mu_B H/T)$ in the expressions for the depolarization rate constants α_{ex} (2.18) and α_{λ} (3.10).

At higher densities, an important role can be assumed by multiparticle processes, which already admit of the appearance of thresholdless depolarization and recombination channels. In the case of depolarization we must take into account the energy-lowering interaction between the particles appearing with opposite spin projection in the states φ_1 or φ_2 with the background (see Ref. 8).

At $T \approx 0$ we are dealing in fact with the energy of "impuriton" excitation in a Bose-condensed gas of particles that is a mixture of hydrogen atoms in the states φ_3 and φ_4 in equal concentrations, or at infra-low temperatures only in the state φ_4 . In the former case the interaction of the particles in the state φ_1 and φ_2 with a mixed Bose condensate leads to the appearance of two types of spin excitations with energies

$$\epsilon_q^{(1)} \approx \hbar^2 q^2 / 2M + 2\mu_B H, \quad (6.1)$$

$$\epsilon_q^{(2)} \approx \frac{\hbar^2 q^2}{2M} + 2\mu_B H - \frac{2\pi\hbar^2}{M} (a_r - a_s) n \quad (6.2)$$

($q \rightarrow 0$). If the background consists of particles in the state φ_4 , then the excitation energy in the presence of an "impurity" particle in the state φ_2 is determined by Eq. (6.2), and in the presence of a particle in the state φ_1 it is determined by Eq. (6.1).

It follows from (6.2) that the depolarization process continues to have a threshold so long as the inequality

$$2\pi\hbar^2 (a_r - a_s) n / M < 2\mu_B H \quad (6.3)$$

is satisfied.

Relations (6.2) and (6.3) differ radically from those obtained by Berlinsky⁸ (see also Ref. 9). The reason is that Berlinsky used implicitly the assumption that the pair correlation functions of particles with parallel and antiparallel spins are equal.

The criterion (6.3) turns out to be much less stringent than Berlinsky's result. It is satisfied with a large margin for such densities as 10^{21} cm⁻³, when the corrections of higher order in the density can still be neglected.

If we confine ourselves to densities $n \leq 10^{21}$ cm⁻³, then the multiparticle effects will be actually caused only by ternary collisions. In ternary collisions of polarized atoms, a thresholdless process corresponding to simultaneous depolarization and recombination is possible. This process consists of a transition of the particles to a bound singlet molecular state with high degree of vibrational excitation. The binding energy released in this case is carried away by a third particle ($|E_{vj}| > 2\mu_B H$). This process can take place both in exchange and in dipole-dipole interactions. Since the spin state of the system must be altered by the collision process, the rate of this process should be slow compared with the rate of the ordinary three-particle recombination.

7. THRESHOLDLESS THREE-PARTICLE RECOMBINATION IN EXCHANGE INTERACTION

In this section we consider the exchange recombination channel. When three polarized atoms collide, a transition of a pair of particles into a bound singlet state takes place in this case only if simultaneous allowance is made for the exchange and hyperfine interactions. The structure of the Hamiltonians of the

exchange of hyperfine interactions predetermines the conservation, in the result of this process, of the projection of the total spin (electron and nuclear) of all three particles, as well as the fact that the projection of the electron spin changes by not more than unity. By virtue of this circumstance, only the following transitions are possible:

$$\begin{aligned} \{444\} &\rightarrow \begin{cases} \text{paramolecule } + \{4\} \\ \text{orthomolecule } (M_I = 0) + \{4\}, \\ \text{orthomolecule } (M_I = 1) + \{3\}, \end{cases} \\ \{344\} &\rightarrow \begin{cases} \text{paramolecule } + \{3\} \\ \text{orthomolecule } (M_I = -1) + \{4\}, \\ \text{orthomolecule } (M_I = 0) + \{3\} \end{cases} \\ \{334\} &\rightarrow \text{orthomolecule } (M_I = -1) + \{3\} \end{aligned} \quad (7.1)$$

(M_I is the projection of the total nuclear spin of the molecule).

Regarding the potential energy of the interaction as the sum of paired interactions, we write down the amplitude of the transition of particles 1 and 2 into a bound state (ν, j) with acquisition by the third particle of a momentum q_f relative to the mass center of the produced molecule, in the form

$$f = -\frac{M'}{2\pi\hbar^2} \sum_{\xi, \eta} \int dR dr \exp(-iq_f r) \Psi_{\nu j}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) \varphi_{\sigma_f}(\xi_3, \eta_3) \times (\hat{V}(r_{13}) + \hat{V}(r_{23})) \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i). \quad (7.2)$$

This equation is obtained directly within the framework of ordinary inelastic-scattering theory. Here $\mathbf{R} = \mathbf{R}_{12}$, \mathbf{r} is the distance from the third particle to the mass center of the quasimolecule (1-2), ξ_i and η_i are the set of spin variables of the electrons and nuclei, $M' = (2/3)M$ is the reduced mass of the molecule and of the atom, and σ_f is the projection of the total spin of the third particle in the final state (the value $\sigma_f = 0$ corresponding to the spin wave function φ_4 , while $\sigma_f = -1$ corresponds to the wave function φ_3). The Hamiltonian $\hat{V}(r_{13}) = U_1(r_{13}) + (r_{13})^{-1}(\hat{S}_1 \hat{S}_3 + 1/4)$ describes the interaction of the third particle with the i -th atom of the quasimolecule (1-2). The true wave function $\Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)$ corresponds to three polarized atoms in the input channel, $\Psi_{\nu j}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2)$ and $\varphi_{\sigma_f}(\xi_3, \eta_3)$ are respectively the wave function of the bound state of the molecule and the spin wave function of the third particle in the final state. The hyperfine interaction is included here in the definition of all the functions in (7.2).

The interaction $\hat{V}(r_{13})$ separates effectively in the integral (7.2) a region of relatively short distances r_{13} . This region is separated also in the product $\hat{V}(r_{13}) \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)$. From pure geometric considerations it is clear that the correlation in the relative positions of the particles 2 and 3 plays a minor role in the determination of this product, and to estimate the amplitude of the transition in the limit as $T \rightarrow 0$ we can use the following approximate representation:

$$\hat{V}(r_{13}) \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i) \approx \hat{V}(r_{13}) \times \Psi_{\mathbf{k}_{12} \rightarrow 0}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) \Psi_{\mathbf{k}_{12} \rightarrow 0}(r_{13}) \varphi_{\sigma_f}(\xi_3, \eta_3), \quad (7.3)$$

and analogously for $\hat{V}(r_{23}) \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)$ (σ_i is the

projection of the total spin of the third particle in the initial state). The reason why the relative motion of the third particle and of the i -th atom is described in this relation by a triplet wave function is the small value of the hyperfine interaction compared with the exchange interaction in the region of the effective interaction.

We determine now the amplitude of the transition in an approximation linear in the hyperfine interaction. To this end we use in the (7.2) and (7.3) wave functions determined within the framework of perturbation theory in \hat{H}_{hf} . We begin with consideration of the formation of a paramolecule (even j) in a collision of three particles in a state φ_4 [see (2.1)]. In this case the wave functions take the form

$$\Psi_{\nu j}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) = \Psi_{\nu j}(\mathbf{R}) \chi_s(\xi_1, \xi_2) \chi_s(\eta_1, \eta_2) + \frac{A}{2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \frac{\langle \Psi_{\mathbf{k}'}^{(t)} | \Psi_{\nu j} \rangle}{|E_{\nu j} - \epsilon_{\mathbf{k}'} - 2\mu_B H|} \Psi_{\mathbf{k}'}^{(t)}(\mathbf{R}) \chi_{s-1}(\xi_1, \xi_2) \chi_{t1}(\eta_1, \eta_2); \quad (7.4)$$

$$\Psi_{\mathbf{k}_{12}}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) = \Psi_{\mathbf{k}_{12}}^{(t)}(\mathbf{R}) \chi_{s-1}(\xi_1, \xi_2) \chi_{t1}(\eta_1, \eta_2) + \kappa \Psi_{\mathbf{k}_{12}}^{(s)}(\mathbf{R}) \chi_s(\xi_1, \xi_2) \chi_s(\eta_1, \eta_2) - \kappa \Psi_{\mathbf{k}_{12}}^{(s)}(\mathbf{R}) \chi_{t0}(\xi_1, \xi_2) \chi_{t0}(\eta_1, \eta_2)$$

$$+ \kappa \int \frac{d\mathbf{k}'}{(2\pi)^3} \frac{\langle \Psi_{\mathbf{k}'}^{(s)} | \Psi_{\mathbf{k}_{12}} \rangle}{1 + \epsilon_{\mathbf{k}'} / 2\mu_B H} \Psi_{\mathbf{k}'}^{(s)}(\mathbf{R}) \chi_s(\xi_1, \xi_2) \chi_s(\eta_1, \eta_2)$$

$$- \frac{A}{2} \sum_{\sigma_f, \sigma_f'} \frac{\langle \Psi_{\sigma_f, \sigma_f'}^{(t)} | \Psi_{\mathbf{k}_{12}} \rangle}{|E_{\sigma_f, \sigma_f'} - 2\mu_B H|} \Psi_{\sigma_f, \sigma_f'}(\mathbf{R}) \chi_s(\xi_1, \xi_2) \chi_s(\eta_1, \eta_2). \quad (7.5)$$

The overlap integrals $\langle \Psi_{\mathbf{k}'}^{(t)} | \Psi_{\nu j} \rangle$ and $\langle \Psi_{\mathbf{k}'}^{(s)} | \Psi_{\mathbf{k}_{12}} \rangle$ are defined here in the usual manner, χ_s and χ_{tm} are the singlet and triplet wave functions for the electron and nuclear spins of the quasimolecule (1-2) and m is the spin projection in the triplet state. The wave function of the bound state contains also increments with electron-spin projection equal to 0 and 1. In the approximation linear in the hyperfine interaction, however, these increments make no contribution to the transition matrix element, and are not taken into account in (7.4).

The leading term in the considered transition amplitude is connected with the admixture of the singlet state in the function $\Psi_{\mathbf{k}_{12}}$ on account of the homogeneous action of the hyperfine Hamiltonian [the second term in (7.5)]. When the initial energy of the particles tends to zero, we can set the total angular momentum of all three particles and the angular momentum of the recombining pair in the initial state equal to zero. In this case, taking (2.11) into account, we have

$$\Psi_{\mathbf{k}_{12} \rightarrow 0}^{(s)}(\mathbf{R}) = \frac{1}{2^{3/2} R} \varphi_s(R), \quad \Psi_{\mathbf{k}_{12} \rightarrow 0}^{(t)}(\mathbf{R}) = \frac{1}{2^{3/2} R} \varphi_t(R), \quad (7.6)$$

$$\Psi_{\mathbf{q} \rightarrow 0}^{(s)}(r_{13}) = \frac{1}{2r_{13}} \varphi_s(r_{13})$$

(the numerical coefficients are different here because the nuclei in the recombining pair are identical). Then, integrating over the angles in (7.2) and summing over the spin variables in explicit form, as well as recognizing that the amplitude is tripled on account of the identity of the initial spin states of the atoms, we obtain

$$\tilde{f}_{vj}^{(p)} = f_{(iii)}^{(p)} \approx -8 \cdot 2^{1/2} \pi \kappa Y_{jm}^* \left(\frac{q_l}{q_l} \right) R_0 a_0^{3/2} A_{vj}^{(p)} J_{vj}^{(p)}, \quad (7.7)$$

where m_j is the projection of the angular momentum j in the bound state (we assume the volume of the system to be equal to unity);

$$A_{vj}^{(p)} = \frac{1}{a_0^{3/2}} \int_0^\infty \chi_{vj}(R) \varphi_v(R) \mathcal{F}_j \left(\frac{q_l R}{2} \right) dR, \quad (7.8)$$

$$J_{vj}^{(p)} = \frac{M}{q_l R_0 \hbar^2} \int_0^\infty \varphi_l(r) \left(U_l(r) + \frac{\Delta(r)}{4} \right) \sin(q_l r) dr. \quad (7.9)$$

The correction to the wave function of the bound state, which is proportional to the hyperfine-interaction constant A and is due to the admixture of states of the continuous spectrum [the second term in (7.4)], and conversely, the correction due to the bound states to the wave function of the continuous spectrum [the last term in (7.5)], add to the transition amplitude a contribution which is small compared with (7.7) in the ratio $2 \mu_B H / |E_{vj}|$. In the first case this can be verified by leaving out ϵ_{κ} from the denominator of the integrand (the characteristic value ϵ_{κ} is less than $|E_{vj}|$), after which the expression for the corresponding amplitude can be greatly simplified.

There is no explicit small parameter in the fourth term of (7.5). Direct calculations show, however, that the contribution from this term to the amplitude of the transition is likewise small compared with (7.7). It must be emphasized that these conclusions remain in force also when other variants of the transitions are considered. Realistically, therefore, when determining the transition amplitude, account need be taken in the wave function of the continuous spectrum of only the corrections that correspond to the second and third terms in (7.5).

We now obtain the amplitude for the production of the orthomolecule (odd j). Here we must already distinguish between cases corresponding to different values of the projection of the nuclear spin of the molecule. It is easily understood that the triplet increment to the wave function of the recombining pair [the third term in (7.5)] leads to formation of an orthomolecule with $M_I = 0$. Explicit calculation of (7.2) yields then

$$\tilde{f}_{vj}^{(or)} = f_{(iii)}^{(or)}(M_I=0) \approx -8 \cdot 2^{1/2} \pi \kappa Y_{jm}^* \left(\frac{q_l}{q_l} \right) R_0 a_0^{3/2} A_{vj}^{(or)} J_{vj}^{(or)}. \quad (7.10)$$

Here

$$A_{vj}^{(or)} = \frac{1}{a_0^{3/2}} \int_0^\infty \chi_{vj}(R) \varphi_l(R) \mathcal{F}_j \left(\frac{q_l R}{2} \right) dR, \quad (7.11)$$

$$J_{vj}^{(or)} = \frac{M}{4q_l R_0 \hbar^2} \int_0^\infty \varphi_l(r) \Delta(r) \sin(q_l r) dr. \quad (7.12)$$

Actually, expression (7.3) contains one more correction proportional to κ . It is due to the form of the spin wave function of the third particle $\varphi_4(\xi_3, \eta_3)$. Allowance for this correction leads to a transition wherein the third particle has in the final state a spin configuration $\varphi_3(\xi_3, \eta_3)$, while the orthomolecule turns

out to be in a state with a nuclear-spin projection $M_I = 1$. The corresponding amplitude is calculated in analogy with (7.10):

$$f_{(iii)}^{(or)}(M_I=1) = -2^{1/2} \tilde{f}_{vj}^{(or)}. \quad (7.13)$$

If one of the colliding particles is in a state φ_3 , and the two others in a state φ_4 , then only the latter can form a paramolecule. The third particle remains in the state φ_3 , and we have for the transition amplitude

$$f_{(iii)}^{(p)} = 1/3 \tilde{f}_{vj}^{(p)}. \quad (7.14)$$

The atoms in the initial spin states φ_3 and φ_4 can form at $T \rightarrow 0$ only an orthomolecule. This is easily established from the form of their paired wave function

$$\begin{aligned} \Psi_{\mathbf{k}_n}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) = & 2^{-1/2} \Psi_{\mathbf{k}_n}^{(1)}(\mathbf{R}) \chi_{l-1}(\xi_1, \xi_2) \chi_{l0}(\eta_1, \eta_2) \\ - & 2^{-1/2} \Psi_{\mathbf{k}_n}^{(2)}(\mathbf{R}) \chi_{l-1}(\xi_1, \xi_2) \chi_l(\eta_1, \eta_2) - 2^{-1/2} \kappa \Psi_{\mathbf{k}_n}^{(3)}(\mathbf{R}) \chi_{l0}(\xi_1, \xi_2) \chi_{l-1}(\eta_1, \eta_2) \\ & + 2^{-1/2} \kappa \Psi_{\mathbf{k}_n}^{(4)}(\mathbf{R}) \chi_s(\xi_1, \xi_2) \chi_{l-1}(\eta_1, \eta_2). \end{aligned} \quad (7.15)$$

The formation of a paramolecule can be connected only with the second term in (7.15), with account taken of the correction, proportional to κ , to the spin wave function of the third particle. The expansion of the coordinate wave function $\Psi_{\mathbf{k}_n}^{(1)}(R)$ in spherical harmonics then includes only odd j , and the transition amplitude contains, compared with the previously obtained ones, an extra power of the small initial momentum. The same smallness is possessed also by the orthomolecule-production amplitude connected with the singlet correction [the last term in (7.15)].

The transition that leads to formation of an orthomolecule with projection $M_I = -1$ is connected with the third term in (7.15). Doubling the transition amplitude (7.2), since two {3, 4} pairs can recombine, we obtain

$$f_{(iii)}^{(or)}(M_I=-1) = -2^{1/2} \tilde{f}_{vj}^{(or)} / 3. \quad (7.16)$$

The formation of an orthomolecule with projection $M_I = 0$ can take place when particles recombine in states φ_3 and φ_4 on account of the increment to the spin wave function of the third particle. A similar transition takes place also when two particles recombine in a state φ_4 [the corresponding amplitude is $1/3$ the value of (7.10)]. Adding both amplitudes we have

$$f_{(iii)}^{(or)}(M_I=0) = -\tilde{f}_{vj}^{(or)} / 3. \quad (7.17)$$

In principle, orthomolecules with projections $M_I = -1$ accompanied by a departure of a third particle in the state φ can be produced in the {334} collision. Such a transition can take place both upon recombination of particles in the states φ_3 and φ_4 , and upon recombination of two particles in the state φ_3 . In the limit at $T \rightarrow 0$, when the singlet increment to (7.15) can be neglected, the corresponding amplitudes are equal in magnitude and opposite in sign, so that this transition does not take place.

We use now the usual connection between the amplitude and the probability of the inelastic transition. Taking into account the paramolecule production amplitudes (7.7) and (7.14) and the orthomolecule pro-

duction amplitude (7.10), (7.13), (7.16), and (7.17), and allowing for the relative concentrations of the particles $c_{3,4}$ in the states φ_3 and φ_4 , we obtain after summing over the projections m_j and M_I for the summary transition probability

$$W = \sum_{v,j} \frac{\hbar q_j m^2}{M'} (2j+1) \times \frac{1}{18} (3c_3^2 + c_4^2) \int [|\bar{f}_{vj}^{(p)}|^2 + 3|\bar{f}_{vj}^{(or)}|^2] dO_{q_j} \quad (7.18)$$

(naturally, for each j either $\bar{f}_{vj}^{(p)}$ or $\bar{f}_{vj}^{(or)}$ is different from zero).

Substituting in (7.18) the expressions (7.7) and (7.10), we obtain directly

$$W^{(ex)} \approx \frac{32}{3} \pi^2 \kappa^2 (\hbar a_0^2 n / MR_0) (n R_0^3) (3c_3^2 + c_4^2) \gamma_{ex}(H), \quad (7.19)$$

$$\gamma_{ex}(H) = \sum_{v,j} (2j+1) [2 - (-1)^j] \times (q_f a_0) |A_{vj}(H) J_{vj}^{(ex)}(H)|^2. \quad (7.20)$$

In expressions (7.18)–(7.20), the value of the final momentum q_f is determined by the energy-conservation law

$$3\hbar^2 q_f^2 / 4M = |E_{vj}| - 2\mu_B H, \quad (7.21)$$

which predetermines its dependence on v , j , and H . The overlap integrals $A_{vj}(H)$ and $J_{vj}(H)$ are determined by relations (7.8) and (7.9) for even j and by (7.11) and (7.12) for odd j , and depend on the magnetic field via q_f .

We compare now the results with the probability of exchange depolarization in the pair collision (2.17) and (2.18). We must note primarily the absence from (7.19) of a factor that depends exponentially on the temperature. This is due to the thresholdless character of the considered three-particle process. It is important that in this case the characteristic time of the decay of the polarized state remains finite as $T \rightarrow 0$.

Expression (7.19) contains the usual small factor nR_0^3 . On the other hand, analysis of the factor $\gamma_{ex}(H)$ calls for a direct calculation of the overlap integrals. Recombination takes place most effectively in the state with the maximum vibrational quantum number $v=14$, to which there correspond in the discrete spectrum four rotational sublevels with $0 \leq j \leq 3$. By way of illustration, Table I lists the overlap integrals at $H=10^5$ Oe. From the presented data it is seen that the modulus A_{vj} of the overlap integral changes little for the recombining pair with changing j . Moreover, it changes little also in a wide range of the magnetic field. On the contrary, the overlap integral $J_{vj}^{(ex)}$ for

TABLE I.

j	$ E_{vj} $, K Ref. 18	$A_{vj}(H)$	$A_{vj}(2H)$	$J_{vj}^{(ex)}(H)$	$J_{vj}^{(d)}(H)$	$J_{vj}^{(d)}(2H)$
0	206	1.3	1.4	$-5 \cdot 10^{-2}$	—	—
1	181	0.7	0.9	-10^{-2}	-10^{-2}	$-1.2 \cdot 10^{-2}$
2	134	-0.8	-0.9	-0.1	—	—
3	70	1.2	0.9	0.4	$2.5 \cdot 10^{-2}$	$6.5 \cdot 10^{-2}$

the third particle turns out to be very sensitive to the value of j . The recombination probability is determined in fact by the transitions to the level with $j=3$. In this case $\gamma_{ex}(H)$ turns out to be larger than unity.

In contrast to A_{vj} , the integral $J_{vj}^{(ex)}$ is sensitive to the value of the magnetic field. With increasing H , a tendency of $|J_{vj}^{(ex)}|$ to decrease is observed, and this predetermines the appearance, in the expression for the reciprocal decay time of the polarized state, of an additional dependence on the magnetic field, besides the factor $\kappa^2 \sim 1/H^2$. This decrease is effectively connected with decrease of the parameter $q_f R_{eff}$ (R_{eff} is the characteristic interaction radius) with increasing H and with the onset of a situation of the Ramsauer-effect type.

The fact that the factor $\gamma_{ex}(H)$ does not produce additional smallness in (7.19) compared with (2.18) is unexpected. This result is explained by the fact that in the course of the paired exchange polarization an abrupt decrease took place in the cross section as a result of the anomalous shortening of the scattering length in the triplet state ($a_t \ll R_0$). There is no such effect in the three-particle process, and linear scales of the order of R_0 are restored.

From (7.19) we get for the reciprocal decay time of a polarized gas in the process under consideration, at $c_3 = c_4$, the following estimate:

$$1/\tau_{ex}^{(3)} \approx 3 \cdot 10^{-33} \kappa^2 b_{ex}(H) n^2 c^{-1}. \quad (7.22)$$

At $H=10^5$ Oe, the factor $b_{ex}(H)=1$. With increasing H , in the interval from $5 \cdot 10^4$ to $1.5 \cdot 10^5$ Oe, it decreases monotonically from 2 to 0.3.

Attention must be called to the fact that according to (7.18) and (7.19) the probability of decay of the polarized gas depends decisively on the density of the particles in the state φ_4 . Missing from these expressions is not only a term proportional to c_3^3 , as is physically obvious, but also a term proportional to $c_3^2 c_4$ (it appears only at a finite temperature). Therefore the time $\tau_{ex}^{(3)}$ increases like $1/c_4^2$ with decreasing c_4 .

8. DIPOLE THREE-PARTICLE RECOMBINATION

Dipole-dipole interaction can also lead to simultaneous depolarization and recombination in ternary collision of polarized atoms. Just as in the case of paired depolarization (see Sec. 3), the hyperfine interaction can be left out when this process is considered.

For the amplitude of a transition in which particles 1 and 2 produce a molecule in a mixed state and particle 3 goes off with a momentum q_f relative to the mass center of this molecule, we use Eq. (7.2) as before. Now, however, we must add to the Hamiltonian $\hat{V}(r_{i3})$ the Hamiltonian $\hat{V}_d(r_{i3})$ (3.1) of the dipole interaction, and the true wave function $\Phi(R, r, \xi_i, \eta_i)$ must be determined with allowance for the dipole-dipole interaction. In the approximation linear in this interaction, it is convenient to represent the transition amplitude as a sum of two terms:

$$f_1^d = f_1^d + f_2^d; \\ f_1^d = -\frac{M'}{2\pi\hbar^2} \sum_{\xi_i, \eta_i} \int d\mathbf{R} d\mathbf{r} \exp(-i\mathbf{q}_f \mathbf{r})$$

$$\times \Psi_{vj}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) \varphi_{\nu_j}(\xi_3, \eta_3)$$

$$\times [\hat{V}_d(r_{13}) + \hat{V}_d(r_{23})] \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i), \quad (8.1)$$

$$f_2^d = -\frac{M'}{2\pi\hbar^2} \sum_{\xi_i, \eta_i} \int d\mathbf{R} d\mathbf{r} \exp(-i\mathbf{q}_f \mathbf{r}) \Psi_{vj}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) \varphi_{\nu_j}(\xi_3, \eta_3)$$

$$\times [\hat{V}_d(r_{13}) + V(r_{23})] [\Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i) - \Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)]. \quad (8.2)$$

Here $\Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)$ is the true wave function with the dipole-dipole interaction neglected. No account is taken in (8.1) and (8.2) of the increment due to the dipole interaction to the wave function of the bound state, since it makes no contribution to the transition matrix element.

We find first the amplitude f_1^d . Since neglect of H_{hf} leads in the considered process to conservation of the nuclear spin, only orthomolecules can be produced in the {333} and {444} collisions. A paramolecule can be produced only by particles in the states φ_3 and φ_4 . For this purpose, however, it is necessary that the initial angular momentum of the recombining pair be odd and this, as already noted, leads to vanishing of the transition amplitude as $T \rightarrow 0$.

In the calculation of (8.1) we retain the approximate representation (7.3) with $\hat{V}(r_{13})$ replaced by $\hat{V}_d(r_{13})$, although it is possible that in the case of a dipole-dipole interaction this approximation is somewhat worse. A triplet quasimolecule wave function enters in this case in (7.3). Using the limiting values of the wave functions (7.6) and summing (7.2) over the spin variables and integrating over the angles, we obtain for the amplitude of the transition without change of the spin state of the third particle in the {444} collision (taking into account the tripling of the amplitude because the particles are identical)

$$\tilde{f}_{vj}^d = f_{1(444)}^d(M_I=1) \approx -24\pi \left(\frac{8\pi}{15}\right)^{1/2} \frac{\mu_B^2 M}{\hbar^2} a_0^{3/2} \\ \times Y_{2-1}\left(\frac{q_f}{q_f'}\right) Y_{20}^* \left(\frac{q_f}{q_f'}\right) A_{vj}^{(or)} J_{vj}^{(d)}, \quad (8.3)$$

where

$$J_{vj}^{(d)} = \int_0^{\pi} \varphi_i(r) \mathcal{F}_2(q_f r) \frac{dr}{r^2}, \quad (8.4)$$

and q_f is specified in accordance with (7.20). Expression (8.3) is given only for odd j .

We obtain analogously an expression for the amplitude of the transition accompanied by a rotation of the electron spin of the third particle:

$$\tilde{f}_{vj}^d = f_{1(444)}^d(M_I=1) \approx 48\pi \left(\frac{8\pi}{15}\right)^{1/2} \frac{\mu_B^2 M}{\hbar^2} a_0^{3/2} \\ \times Y_{2-2}\left(\frac{q_f}{q_f'}\right) Y_{20}^* \left(\frac{q_f}{q_f'}\right) A_{vj}^{(or)} J_{vj}^{(d)}. \quad (8.5)$$

In this expression q_f is determined already from the relation

$$3\hbar^2 q_f^2 / 4M = |E_{vj}| - 4\mu_B H. \quad (8.6)$$

For other collision variants, we have

$$f_{1(333)}^d(M_I=-1) = \tilde{f}_{vj}^d, \quad f_{1(344)}^d(M_I=1) = f_{1(334)}^d(M_I=-1) = 1/2 \tilde{f}_{vj}^d, \quad (8.7) \\ f_{1(344)}^d(M_I=0) = f_{1(334)}^d(M_I=0) = 2^{1/2} \tilde{f}_{vj}^d / 3.$$

Exactly the same relations are obtained also for the amplitudes of a transition with change of the state of the third particle f_1^d .

Expression (8.2) is perfectly analogous in structure to (7.2), and when using for its calculation the same approximation (7.3) we should replace in the latter the paired wave function $\Psi_{k_{12} \rightarrow 0}$ by the correction to this function due to the dipole-dipole interaction. Direct calculation of f_2^d has shown that this amplitude is substantially lower than f_1^d , and we shall disregard it in the estimates of the transition probability.

We note that in principle we could have treated all three dipole interactions as a perturbation within the framework of the distorted-wave method. If the wave function of the final state, taking into account the large value of q_f , is approximately represented here in the form

$$\Psi_{vj}(\mathbf{R}, \xi_1, \xi_2, \eta_1, \eta_2) \exp(i\mathbf{q}_f \mathbf{r}),$$

we would obtain the same result, since our choice of the wave function $\Phi(\mathbf{R}, \mathbf{r}, \xi_i, \eta_i)$ in the form (7.3) would cause the matrix element of $\hat{V}_d(r_{12})$ to vanish. The ensuing inaccuracy turns out to be not very large, since the small distances r_{13} and r_{23} are practically excluded upon integration because of the behavior of the triplet wave function φ_i .

Using the relations obtained for the transition amplitudes [see (8.3), (8.5) and (8.7)], and taking into account recombination channels with and without spin flip of the third particle, we get for the transition probability [cf. (7.18)]

$$W^{(d)} = \sum_{vj} \frac{\hbar q_f n^2}{M'} (2j+1) \frac{1}{6} (c_1^2 + c_3 c_1^2 + c_3^2 c_1 + c_3^2) \\ \times \int [|\tilde{f}_{vj}^d|^2 + \frac{4q_f'}{q_f} |\tilde{f}_{vj}^d|^2] dO_{q_f}. \quad (8.8)$$

The summation here is only over odd j , while q_f and q_f' are determined in accordance with (7.21) and (8.6).

Substituting in (8.8) expressions (8.3) and (8.5), we obtain

$$W^{(d)} \approx \frac{96\pi^2}{5} \left(\frac{\mu_B^2 M}{\hbar^2}\right)^2 \frac{\hbar}{MR_0} n(nR_0^3) (c_1^2 + c_3 c_1^2 + c_3^2 c_1 + c_3^2) \gamma_d(H), \quad (8.9)$$

$$\gamma_d(H) = \left(\frac{a_0}{R_0}\right)^2 \sum_{vj} (2j+1) \{q_f a_0 [A_{vj}(H) J_{vj}^{(d)}(H)]^2 \\ + 4q_f' a_0 [A_{vj}(2H) J_{vj}^{(d)}(2H)]^2\} \quad (8.10)$$

[the overlap integrals A_{vj} and J_{vj}^d are determined by formulas (7.11) and (8.4)]. The recombination process goes in this case effectively to the same levels as in the case of exchange interaction, the only difference being that now j takes on only odd values. By way of illustration, Table I lists the overlapping integrals J_{vj}^d in the expression for $\gamma_d(H)$ at $H = 10^5$ Oe. Again, the recombination to a level with $j=3$ is decisive. An important role is played here by transitions with simultaneous spin flip of the third particle.

The coefficient $\gamma_d(H)$ (8.10) amounts to $\sim 10^{-3}$ and is smaller by more than two orders of magnitude than the coefficient $\gamma_{ex}(H)$ (7.21). Therefore the role of the dipole mechanism in the three-particle recombination process is greatly decreased compared with the paired depolarization process. The reciprocal lifetime of the polarized gas with respect to dipole recombination is

$$1/\tau_d^{(3)} \approx 2 \cdot 10^{-19} b_d(H) n^2 \text{ sec}^{-1} \quad (c_s = c_i, b_d(H=10^5 \text{ Oe})=1) \quad (8.11)$$

it turns out to be much less than $1/\tau_{ex}^{(3)}$ (7.22) at $H = 10^5 \text{ Oe}$.

The factor $b_d(H)$ has an inverse dependence on the magnetic field compared with $b_{ex}(H)$, namely, it increases with H and changes from 0.3 to 2 in the interval from $5 \cdot 10^4$ to $1.5 \cdot 10^5 \text{ Oe}$. At larger values of H it begins to decrease. The principally different character of the dependences of $\tau_{ex}^{(3)}$ and $\tau_d^{(3)}$ on the magnetic field causes the channels of the exchange in dipole recombination to become rapidly equalized in velocity with increasing H .

We note one more circumstance. Direct calculations have shown that the modulus of the overlap integral $J_{v_j}^{(d)}$ decreases strongly with increasing final momentum q_f . Therefore the model assumed by us seems to overestimate the probability $W^{(d)}$, since the real potential of the $H-H_2$ interaction has a well that increases the effective value of the final momentum in the interaction region.

Thus, on account of simultaneous depolarization and recombination in the process of ternary collision of polarized atoms, the decay time of the metastable polarized gas phase remains finite as $T \rightarrow 0$. This restricts in principle the attainable values of the density. As follows from the results, at $H = 10^5 \text{ Oe}$ a lifetime of the order of hours is possible only up to densities $n \sim (1-2) \cdot 10^{17} \text{ cm}^{-3}$. In the limiting strong field $H \sim (2-2.5) \cdot 10^5 \text{ Oe}$ such a lifetime corresponds to $n \sim 10^{18} \text{ cm}^{-3}$.

9. ROLE OF SURFACE EFFECTS

When considering the gas phase at low temperature, we encounter in principle the strong role of the surface effects. Indeed, if the surface density of the adsorbed gas becomes large, then thresholdless depolarization and recombination processes, similar to the processes considered in the preceding section, come immediately into play. The role of the third body, in particular, can be assumed in this case by the surface. The most troublesome here is the thresholdless production of spin excitations in paired depolarization, which results from violation of an inequality similar to (6.3) if the coating of the surface is close to a monolayer.

At $T=0$ the chemical potential of the adsorbed atoms is determined by the value $\bar{\epsilon}_0$, renormalized on account of the interaction on the surface, of the ground state (ϵ_0) in the adsorption well (cf. Ref. 19):

$$\mu_s = \bar{\epsilon}_0 = \epsilon_0 + \delta 2\pi \hbar^2 n_s / M. \quad (9.1)$$

Here n_s is the surface density of the adsorbed atoms, and $\delta \sim 1$ is a dimensionless coefficient that depends on the interaction of the atoms with one another and with the surface ($\epsilon_0 < 0$).

The bulk chemical potential has the usual value for a rarefied gas:

$$\mu_v = 4\pi \hbar^2 a_s n / M. \quad (9.2)$$

The number of free places on the surface for polarized hydrogen atoms is approximately equal to

$$n_{s0} \approx 1/\pi R_0^2 \approx 3 \cdot 10^{14} \text{ cm}^{-2}. \quad (9.3)$$

It follows directly from (9.1)–(9.3) that the inequality $n_s < n_{s0}$ at equilibrium ($\mu_s = \mu_v$) at $T=0$ can be satisfied only under the condition $|\epsilon_0| \lesssim 1 \text{ K}$. So low a value of the adsorption energy is known at present only in a single case: on a surface covered with a helium film ($|\epsilon_0| \approx 0.9 \text{ K}$,^{20,21}). In all the remaining cases the lowest value of $|\epsilon_0|$ is of the order of tens of degrees (for example, $\epsilon_0 \sim 40 \text{ K}$ on the surface of molecular hydrogen. The requirement $n_s < n_{s0}$ can then be satisfied only at finite temperatures. Assuming that T is higher than the degeneracy temperature both in the bulk and on the surface, we obtain approximately for the ratio of the surface density to the bulk density in the case of free motion of the atoms over the surface

$$n_s \approx n (2\pi \hbar^2 / MT)^{3/2} \exp(|\epsilon_0|/T). \quad (9.4)$$

If the adsorption is localized, then

$$n_s \approx n n_{s0} (2\pi \hbar^2 / MT)^{3/2} \exp(|\epsilon_0|/T). \quad (9.5)$$

It is easy to conclude from (9.4) and (9.5) that at $T \lesssim 1 \text{ K}$ the formation of a monolayer is unavoidable for all surfaces, except one covered with helium, at all bulk-density values of interest.

It is therefore meaningful to estimate the role of surface effects just for the case of a helium coating. In this case the ratio n_s/n_{s0} remains less than or of the order of 0.1 at all temperatures down to $T=0$ (at $n \lesssim 10^{20} \text{ cm}^{-3}$), so that the question of thresholdless production of collective spin excitations is avoided. The leading decay channel of the polarized phase on the surface is then three-particle recombination with change of the spin state. If the result for the number of acts of bulk recombination of this type per unit time is represented in the form

$$w_v (n R_0)^2 n V = \nu_v V \quad (9.6)$$

(V is the volume of the system), then the total number of recombination due to ternary collisions of adsorbed atoms acts on a surface S can be written in the form

$$w_s (n_s R_0)^2 n_s S = \nu_s S. \quad (9.7)$$

The coefficients w_v and w_s are of the same order of magnitude.

On the helium surface, however, a recombination process is possible with a change of the spin state, wherein the role of the third body is assumed by the helium atoms. This process was observed in experiment.²¹ Since the binding energy of the helium

atoms in the film is small compared with the energy (7.21) transferred in the recombination to the third particle, we have in this case an estimated number of recombination acts

$$\bar{w}_s (n_s R_0^2) n_s S = \bar{v}_s S. \quad (9.8)$$

The quantity \bar{w}_s can differ in principle somewhat from w_s on account of the specifics of the kinematics of the collision and of the difference between the $H\uparrow-H\uparrow$ and $H-He$ interaction potentials. At the same time it is of interest to note that the recombination rate constant obtained experimentally by Hardy *et al.*²² for unpolarized atomic hydrogen in a helium atmosphere at $T \approx 1$ K turned out to be quite close to the value that follows from (7.22), if the factor κ^2 is left out of the latter.

We emphasize that the process of simultaneous depolarization and recombination with participation of the helium atom can be connected only with the exchange mechanism. If one of the particles in the three-particle cluster has zero spin, the dipole-interaction cannot alter the total spin. Consequently dipole recombination with participation of a helium atom turns out to be impossible.

As shown in the preceding section, in an ordinary mixture of hydrogen atoms in spin states φ_3 and φ_4 the strong decay channel is exchange recombination, by virtue of which recombination on the surface should be described by relation (9.8) ($n_s R_0^2 \ll 1$). It is important that if the third particle in the recombination is a helium atom, then the value of the final momentum q_f , which enters in all the overlap integrals, is increased by a factor $\sqrt{2}$. This leads to a weakening of the $b_{\kappa}(H)$ dependence, which becomes additionally weakened by the difficulty of formation of a molecule in a bound state with $j=3$. As a result, the dependence of (9.8) on the magnetic field can be close to κ^2/H^2 . Such a dependence was recently observed for the considered process in experiment.²¹ If we use the surface-recombination rate constant obtained in that reference, then we have for \bar{v}_s as $T \rightarrow 0$ the estimate ($n_s = n_s^{\text{max}} \approx 3 \cdot 10^{13} \text{ cm}^{-3}$): $\bar{v}_s \approx 2 \cdot 10^{18} \text{ 1/cm}^2 \cdot \text{sec}$ ($H = 10^5$ Oe). It is easy to estimate here that surface recombination predominates over the volume recombination up to densities $n \sim 10^{19} \text{ cm}^{-3}$. If we arbitrarily introduce the reciprocal effective decay time $1/\tau_{\text{eff}}$ as the ratio of the number of particles recombining in the bulk and on the surface per unit time to the total number of particles, then it turns out that as $T \rightarrow 0$ the maximum value of τ_{eff} is ~ 0.2 sec. This time decreases both when the density increases and when it decreases from the value 10^{19} cm^{-3} .

The obtained estimates offer evidence that it is practically impossible to reach the Bose condensation region by direct means. It is possible, however, to accumulate a polarized atomic-hydrogen phase by using a finite temperature to which, according to (9.4), the condition $n_s/n_s^{\text{max}} \ll 1$ corresponds. Thus, at $T \approx 0.5$ K we can reach densities $n \sim 10^{17} \text{ cm}^{-3}$, and if $H \sim (2-2.5) \times 10^5$, then also $n \sim 10^{18} \text{ cm}^{-3}$, and we can get τ_{eff} on the order of hours.

The picture changes substantially if the polarized hydrogen atoms are only in the spin state φ_3 . In this case there is no exchange recombination in the volume and on the surface, and the only remaining threshold-less decay channel is dipole recombination. As already noted, the channel of surface recombination with participation of a helium atom is suppressed in this case, and recombination takes place only in the collision of three polarized hydrogen atoms. In this, relation (9.7) is already valid for its rate.

It is important that in the case considered the surface recombination decreases abruptly at $H \sim (0.5-1) \times 10^5$ Oe, both because of the small parameter ($n_s R_0^2$) and because the rate constant (8.11) of the dipole recombination is smaller than the corresponding value for the exchange recombination. Estimates show that if we assume $w_s \approx w_v$ and use relation (8.11), when τ_{eff} reaches in this case a maximum value $\sim 10-100$ sec. The corresponding volume density is $n \sim 3 \cdot 10^{18} \text{ cm}^{-3}$.

We note that any decrease of $|\varepsilon_0|$ leads to a substantial increase of the effective decay time, since $\nu_s \sim |\varepsilon_0|^3$ (in films of the mixture He^3-He^4 the adsorption energy was decreased to 0.6 K—Ref. 21).

The presented estimate of τ_{eff} is obviously approximate because of the inaccurate knowledge of such surface-recombination parameters as w_s and the surface density as $T \rightarrow 0$. At the same time, as already noted in Sec. 8, the rate constant (8.11) of the bulk recombination is apparently overestimated (consequently τ_{eff} is underestimated). As a result, a final assessment of the feasibility in principle of reaching the Bose-condensation region can be made only after greatly refining these parameters. In any case, however, the separation of spin-polarized hydrogen in the state φ_3 is to all appearances optimal.

We note that dipole interaction between the electron spin of one atom and the electron and nuclear spins of another makes possible relaxation of the nuclear spin with a transition of the atom from the state φ_3 into the state φ_4 . An analysis perfectly similar to that in Sec. 3 leads for the reciprocal relaxation time at $T \ll \Delta\varepsilon_0$ ($\Delta\varepsilon_0$ is the energy difference of the atoms in the states φ_3 and φ_4 , and is equal to $5 \cdot 10^{-2}$ K and $H \approx 10^5$ Oe) to the value

$$1/\tau_{\text{rel}} = \alpha_{\text{rel}} n, \quad \alpha_{\text{rel}} \approx 4 \cdot 10^{-22} (1 + \kappa \mu_B / \mu_p)^2 \text{ cm}^3 \cdot \text{sec}, \quad (9.9)$$

(μ_p is the magnetic moment of the proton). On the other hand, if $1 \text{ K} \gtrsim T \gg \Delta\varepsilon_0$, then an additional factor $(T/\Delta\varepsilon_0)^{1/2}$ appears in the expression for α_{rel} .

Thus, if we have a polarized-system decay time on the order of hours, then this mechanism does not change the scale all the way to $n \sim 10^{18} \text{ cm}^{-3}$.

It should be pointed out that as $T \rightarrow 0$ the probability of three-particle exchange recombination is proportional to c_4^2 [see (7.19)]. A similar result is valid also for recombination on a surface with participation of a helium atom. This, in particular, permits the presence of approximately 1% of a component in the state φ_4 .

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