Kinetic Theory of Nonequilibrium Alignment Phenomena in Atomic Vapors

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(Z. Naturforsch. **28 a**, 1543—1553 [1973]; received 7 May 1973)

Nonequilibrium alignment phenomena in gases of polyatomic molecules (Senftleben-Beenakker effect, flow birefringence) have been studied extensively during the last decade. Similar effects should also exist for atoms with nonzero electronic orbital angular momentum. The Waldmann-Snider equation (considered as Boltzmann equation for reacting mixtures) is used to derive an expression for the tensor polarization caused by a flow field in such atomic vapors. As a simple special case ^{2}P-atoms are treated as an effective two level system (fine structure doublet). They can be tensor-polarized in the state with $j=3/2$. An ansatz is made for the nonspherical interaction potential between ^{2}P-atoms. The scattering amplitude is calculated in first order Born approximation which is reasonable for the high temperatures necessary. The relevant cross sections and collision integrals are evaluated. The temperature dependence of the alignment and its order of magnitude are discussed. Although the effect is rather small it should be detectable by optical methods (flow birefringence). The connection of flow birefringence and collisional alignment is elucidated.

Introduction

The non-equilibrium collisional alignment of the rotational angular momenta in a molecular gas is indicated directly by the flow birefringence[1, 2] and indirectly by the influence of magnetic and electric fields on the transport properties — the Senftleben-Beenakker effect[3, 4]. These phenomena have been extensively studied in the last decade from the experimental[5] as well as from the theoretical[6, 7] side. However, several attempts to observe an influence of a magnetic field on the transport properties of monatomic gases failed[8]. This is not surprising because all monatomic gases studied so far consisted of atoms without an orbital electron angular momentum $\hbar \boldsymbol{L}$. For these atoms, e.g. Na or Cs, the electron cloud is spherically symmetric and thus also the interaction potential is essentially spherical if the small magnetic dipole-dipole interaction between the electron spins is disregarded; i.e. the spin is practically not influenced in a scattering process.

The situation should be different for atomic vapors consisting of atoms with non-vanishing orbital angular momentum because then the "shape" of the atom and consequently the interatomic potential is nonspherical. If the fine structure energy splitting is very large compared with $k_{\mathrm{B}} T$ practically all atoms are in the ground state. Then, as far as transport properties are concerned, the atoms can be considered as particles with spin (single level system) provided that the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is nonzero. Here $\boldsymbol{S}$ is the total intrinsic electronic spin operator in units of $\hbar$. Examples of this type would be gases of Tl(^{2}P$_{1/2}$), I(^{2}P$_{3/2}$), Te(^{3}P$_2$) atoms at temperatures below 2500 K. The kinetic theory for gases of particles with spin has been developed a decade ago[9, 10]. No experimental observations of nonequilibrium alignment phenomena, however, have been reported for these gases. This is also true for o-H$_2$ at very low temperatures where only the rotational state $j = 1$ is occupied[11].

The magnitude of nonequilibrium alignment phenomena can be expected to be larger for multiple level systems[12] realized by gases of atoms with a smaller fine structure energy splitting. In particular, the flow birefringence and the Senftleben-Beenakker effect of the viscosity are larger if energetically inelastic collisions occur frequently enough. The Senftleben-Beenakker effect of the heat conductivity is larger if a significant internal energy flux exists. This requires that a considerable fraction of the atoms is in an excited state. The simplest atoms for which a flow birefringence or a Senftleben-Beenakker effect of an observable magnitude can be expected are the ^{2}P atoms: B, Al, Ga. The fine structure energy separation between the ^{2}P$_{1/2}$ ground state and the first excited ^{2}P$_{3/2}$ state is relatively small such that at temperatures above 1000 K a significant fraction (about 50% for Ga at 1600 K) of the atoms is in the $j = 3/2$ state. These

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atoms can be tensor polarized, i.e. the average value (over a single particle distribution) of the irreducible tensor operator $\langle\overline{\boldsymbol{J}\,\boldsymbol{J}}\rangle$ built up from the components of $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ ($L = 1$, $S = 1/2$) is different from zero if a flow velocity field $\boldsymbol{v}(\boldsymbol{x})$ is present. A vector polarization (which also could exist for the $j = 1/2$ particles) cannot occur because it is an axial vector which does not couple (by means of the collisions) to the polar vectors (e.g. heat fluxes) which can exist in a nonequilibrium state because of the parity invariance of the interaction.

A collision induced tensor polarization of ${}^2\mathrm{P}_{3/2}$ atoms has been observed accidentally by Toschek[13] with a beam of Ga atoms emerging from an oven at 1600 K. The alignment decreased with increasing temperature. A detailed analysis of this experiment has not been given. Further experiments on collisional alignment produced by a streaming field, flow birefringence, and field effects on the transport properties of such atomic vapors are desirable. Besides for the gases of ${}^2\mathrm{P}$ atoms mentioned above, a study of nonequilibrium alignment phenomena might be promising for gases of Sc, La (${}^2\mathrm{D}$), O, S, Se (${}^3\mathrm{P}$) and Fe (${}^5\mathrm{D}$).

The present paper deals with the kinetic theory of collisional alignment. The linearized Waldmann-Snider equation[14, 15] is used to derive an expression for the tensor polarization caused by a flow field. In general, one is interested in the atoms with a particular total angular momentum j. Thus, the Waldmann-Snider equation is considered as a quantum mechanical Boltzmann equation for reacting mixtures. The components of the mixture are the atoms in the different j-states. The possibility of reations is contained in the collision term, the reactions consist in a change of j in a collision. It should be noted that a mixture conception of the Waldmann-Snider equation has also been exposed in a paper of Coope and Snider[16] but in their "uncoupled model" these authors neglect the occurence of reactions, i.e. inelastic collisions. In general, this is an appealing but unrealistic simplification. With the help of the moment method[10, 17, 18] the transport relaxation equations governing the alignment problem are derived from the linearized Waldmann-Snider equation. The tensor polarization of the atoms in the state j is proportional to the dimensionless friction pressure tensor in a stationary state. The coefficient of proportionality is determined by a ratio of collision integrals of the linearized Waldmann-Snider collision term. This is explicated in detail for the $j = 1/2$, $3/2$ two level system. The collision integrals depend crucially on that part of the binary scattering amplitude which is connected with the nonsphericity of the interatomic potential. A reasonable ansatz is made for the nonspherical interaction between ${}^2\mathrm{P}$ atoms. The scattering amplitude is calculated in first order Born approximation which may be valid for high enough temperatures and small nonsphericity. The contribution of the magnetic dipole-dipole interaction is negligible; the expressions for the collision integrals can then be simplified considerably. A simple expression is found for the proportionality coefficient mentioned above which is linear in the dimensionless fine structure energy splitting $\Delta E/k_{\mathrm{B}}T$ as well as dependent on the ratio of two effective reorientation cross sections for the tensor polarization which describe elastic and inelastic collisions, respectively. Within the Born approximation (also in distorted wave Born approximation, cf. Ref. [12]) the alignment vanishes if only energetically elastic collisions occur. The temperature dependence of the alignment is discussed and its magnitude is estimated for Ga at 1600 K, 1 Torr and a velocity gradient of $5 \times 10^2\ \mathrm{sec}^{-1}$ (achievable with laminar flow between rotating cylinders). It is of the order of magnitude of 10^{-4}. Thus optical methods like flow birefringence should be used for the detection rather than a Stern-Gerlach experiment. The connection of the irreducible part of the dielectric tensor describing flow birefringence with the tensor polarization is elucidated. Finally some remarks are made on the Toschek experiment.

I. Kinetic Theory of Collisional Alignment

1. Notations, Linearized Waldmann-Snider Equation

Starting point for the kinetic treatment of orientation phenomena in dilute gases is the linearized Waldmann-Snider equation for the deviation Φ^j of the nonequilibrium distribution matrix f^j of the particles in the state j from the equilibrium distribution:

$$f^j(t, \boldsymbol{x}, \boldsymbol{c}, \boldsymbol{J}) = f_0^j(c, J^2)(1 + \Phi^j)\,. \qquad (1.1)$$

The nonequilibrium distribution operator f^j is defined by

$$f^j(t, \boldsymbol{x}, \boldsymbol{c}) = P^j f(t, \boldsymbol{x}, \boldsymbol{c}, \boldsymbol{J})\, P^j\,, \qquad (1.2)$$

where $\boldsymbol{J}$ is the operator for the total internal angular momentum with eigenstates $|jm\rangle$ of J^2 and J_z and

$$P^j = \sum_m |j\,m\rangle\langle j\,m| \tag{1.3}$$

is the projection operator on the subspace characterized by the eigenvalue $j(j+1)$ of J^2. The equilibrium distribution $f_0{}^j$ is given by

$$\begin{aligned} f_0^j(c) = {} & n_0\, p_j\, (m/2\pi\, k_\mathrm{B}\, T_0)^{3/2} \\ & \cdot \exp\{-m\,c^2/2 k_\mathrm{B}\, T_0\}\, g_j^{-1}\, P^j . \end{aligned} \tag{1.4}$$

In Eq. (1.4), n_0 is the equilibrium particle number density and $g_j = 2j+1$ is the degree of degeneracy of the level assigned with j, and

$$p_j = g_j \exp\{-E(j)/k_\mathrm{B}\, T_0\} / \sum_j g_j \exp\{-E(j)/k_\mathrm{B}\, T_0\} \tag{1.5}$$

is the occupation probability of the state with quantum number j in equilibrium. Clearly, the equilibrium particle density $n_0(j)$ of atoms in the state j is

$$n_0(j) \equiv n_0\, p_j = \mathrm{tr}_j \int f_0^j(c)\, \mathrm{d}^3 c\,, \tag{1.6}$$

where "tr_j" denotes the trace over the magnetic quantum numbers m and where $\mathrm{tr}_j\, P^j = g_j$ has been used.

The linearized Waldmann-Snider equation is written as

$$\partial \Phi^{j_1}/\partial t + \boldsymbol{c}_1 \cdot (\partial \Phi^{j_1}/\partial \boldsymbol{x}) + \omega(\Phi)^{j_1} = 0\,. \tag{1.7}$$

The linearized collision term $\omega(\Phi)^{j_1}$ can be decomposed in the mixture form:

$$\omega(\Phi)^{j_1} = \sum_{j_2} n_0(j_2)\, \omega(\Phi)^{j_1}_{j_2}\,, \tag{1.8}$$

where $\omega(\Phi)^{j_1}_{j_2}$ is still an operator acting in j_1-space (the operator property is denoted by a superscript j_1) but a c-number in j_2-space (denoted by subscript j_2). It is expressed by

$$\begin{aligned} \omega(\Phi)^{j_1}_{j_2} = {} & -(1/n_0)\, \mathrm{tr}_{j_2} \int \mathrm{d}^3 c_2\, f_0(c_2)\, g_{j_2}^{-1} \\ & \cdot \Big\{ \sum_{j_1' j_2'} \int a^{j_1 j_2,\, j_1' j_2'} (\Phi^{j_1'} + \Phi^{j_2'})\, a^{+ j_1' j_2',\, j_1 j_2}\, g'\, \mathrm{d}^2 e' \\ & - (h/i\, m_{12})\, [a(0)^{j_1 j_2,\, j_1 j_2} (\Phi^{j_1} + \Phi^{j_2}) \\ & - (\Phi^{j_1'} + \Phi^{j_2'})\, a(0)^{+ j_1 j_2,\, j_1 j_2}] \Big\} . \end{aligned} \tag{1.9}$$

In Eq. (1.9) $f_0(c_2)$ is defined by the equation

$$f_0^j(c_2) = f_0(c_2)\, p_j\, g_j^{-1}\, P^j; \quad \Phi^{j_1'} \equiv \Phi^{j_1'}(\boldsymbol{c}_1', t, \boldsymbol{x})\,,$$

etc., and $\boldsymbol{g}' = g' \boldsymbol{e}' = (\boldsymbol{c}_1' - \boldsymbol{c}_2')$ is the relative velocity before the collision (primed quantities always refer to the situation before the collision, the unprimed ones to the situation after the collision). The quantity $a^{j_1 j_2, j_1' j_2'}(g, \boldsymbol{e}, \boldsymbol{e}')$ is the single channel scattering amplitude (matrix with respect to the magnetic quantum numbers) which describes the collision process $j_1' + j_2' \rightarrow j_1 + j_2$. The scattering amplitude in the forward direction is denoted by $a(0)$.

2. Transport-Relaxation Equations

For the treatment of the flow induced alignment the operator Φ^j is expanded into a sum of orthonormal tensors built up from the molecular velocity $\boldsymbol{c}$ and the operator $\boldsymbol{J}$. Their average values are the macroscopic variables appropriate for the problem considered:

$$\begin{aligned} \Phi^j = {} & \mathbf{a}_\eta(j, t, \boldsymbol{x}) : \boldsymbol{\Phi}_\eta(\boldsymbol{c}) \\ & + \mathbf{a}_\mathrm{T}(j, t, \boldsymbol{x}) : \boldsymbol{\Phi}^j_\mathrm{T}(\boldsymbol{J}) + \boldsymbol{a}(t, x) \cdot \boldsymbol{\Phi}(\boldsymbol{c}). \end{aligned} \tag{1.10}$$

The tensors appearing in Eq. (1.10) have the following physical meanings:

$$\begin{aligned} \boldsymbol{\Phi}_\eta(\boldsymbol{c}) &= (m/\sqrt{2}\, k_\mathrm{B}\, T_0)\, \overline{\boldsymbol{c}\,\boldsymbol{c}}\,, \\ \boldsymbol{\Phi}^j_\mathrm{T}(\boldsymbol{J}) &= P^j [\tfrac{2}{15} J^2 (J^2 - \tfrac{3}{4})]^{-1/2}\, \overline{\boldsymbol{J}\,\boldsymbol{J}}\, P^j, \\ \boldsymbol{\Phi}(\boldsymbol{c}) &= \sqrt{m/k_\mathrm{B}\, T_0}\, \boldsymbol{c}\,. \end{aligned} \tag{1.11}$$

Their average values are the macroscopic variables relevant for the flow-induced alignment problem: First, we have

$$\langle \boldsymbol{\Phi}_\eta \rangle_j = \mathbf{a}_\eta(j) = (1/\sqrt{2}\, p_{0j})\, \mathbf{p}(j)\,, \tag{1.12}$$

(p_{0j} is the partial pressure of the component j and $\overline{\mathbf{p}}(j)$ is the friction pressure tensor). The vector

$$\langle \boldsymbol{\Phi} \rangle = \boldsymbol{a} = \sqrt{m/k_\mathrm{B}\, T_0}\, \boldsymbol{v}\,, \tag{1.13}$$

determines the flow velocity which is assumed to be independent of j since it is considered to be produced by some external arrangement (rotating cylinders) and does not couple by means of collisions with other variables. Finally, the tensor

$$\begin{aligned} \langle \boldsymbol{\Phi}_\mathrm{T} \rangle_j &= \mathbf{a}_\mathrm{T}(j) \\ &= [\tfrac{2}{15} j(j+1)(j(j+1) - \tfrac{3}{4})]^{-1/2} \langle \overline{\boldsymbol{J}\,\boldsymbol{J}} \rangle_j \end{aligned} \tag{1.14}$$

is proportional to the tensor polarization $\langle \overline{\boldsymbol{J}\,\boldsymbol{J}} \rangle_j$ of the subset of atoms with total angular momentum j. The tensor polarization is connected with the occupation probabilities of the magnetic substates $N(m)$ by

$$\boldsymbol{h} \cdot \langle \overline{\boldsymbol{J}\,\boldsymbol{J}} \rangle_j \cdot \boldsymbol{h} = \sum_m N(m)\, (m^2 - \tfrac{1}{3} j(j+1))\,, \tag{1.15}$$

where $\boldsymbol{h}$ is a unit vector in the direction of the axis of quantization. The expansion tensors (1.11) are normalized according to

$$\langle \boldsymbol{\Phi}_k \boldsymbol{\Phi}_l \rangle_0 = \delta_{kl}\, \boldsymbol{\Delta}, \qquad \langle \Phi\, \Phi \rangle_0 = \boldsymbol{\delta}\,, \tag{1.16}$$

where $\boldsymbol{\delta}$ is the second rank unit tensor and $\boldsymbol{\Delta}$ is a fourth rank isotropic tensor with elements

$$\Delta_{\mu\nu,\varkappa\lambda} = \tfrac{1}{2}(\delta_{\mu\varkappa}\,\delta_{\nu\lambda} + \delta_{\mu\lambda}\,\delta_{\nu\varkappa}) - \tfrac{1}{3}\,\delta_{\mu\nu}\,\delta_{\varkappa\lambda}$$

which projects out the irreducible part of an arbitrary second rank tensor; $k, l = \eta, T$. The bracket symbol $\langle \cdots \rangle_0$ denotes an equilibrium average

$$\langle \cdots \rangle_0 = (1/n_0(j))\, \mathrm{tr}_j \int f_0{}^j(c)(\cdots)\, \mathrm{d}^3c\,. \tag{1.17}$$

In most treatments of the Senftleben-Beenakker effect[6, 7] in molecular gases macroscopic variables are used which are averages of the quantities used above over the rotational states, e.g.

$$\mathbf{a}_{\mathrm{T}}(t, \boldsymbol{x}) = \sum_j p_j\, \mathbf{a}_{\mathrm{T}}(j, t, \boldsymbol{x})\,. \tag{1.18}$$

Here, however, only averages within a j-subspace appear, i.e. in essence a mixture theory is presented. The atoms with different j could, in principle, be separated in a beam by means of inhomogeneous magnetic or electric fields[19]. Similar considerations regarding the averaging within a j-subset have been made by Coope and Snider[16] but in their "uncoupled model' they neglect the reactions, i.e. the inelastic collisions (where j changes). As we shall see later, this neglect is extremely unrealistic for our case.

Inserting now the expansion, Eq. (1.10), into (1.7), multiplying Eq. (1.7) with the different expansion tensors (1.11), taking the equilibrium average (1.17), observing (1.16) and applying the optical theorem for the scattering amplitude in the collision term (1.9) we obtain the following moment equations (the variables $t, \boldsymbol{x}$ are omitted for simplicity):

$$\frac{\partial \mathbf{a}_\eta(j_1)}{\partial t} + \sqrt{2}\, \overline{\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}} + \{\Omega_{\eta\mathrm{T}}\, \mathbf{a}_{\mathrm{T}}\}_{j_1} + \{\Omega_\eta\, \mathbf{a}_\eta\}_{j_1} = 0\,, \tag{1.19}$$

$$\frac{\partial \mathbf{a}_{\mathrm{T}}(j_1)}{\partial t} + \{\Omega_{\mathrm{T}\eta}\, \mathbf{a}_\eta\}_{j_1} + \{\Omega_{\mathrm{T}}\, \mathbf{a}_{\mathrm{T}}\}_{j_1} = 0\,. \tag{1.20}$$

The moment equation for $\boldsymbol{v}$ is not of interest here. In Eqs. (1.19), (1.20) the following curly bracket symbols have been introduced:

$$\begin{aligned}\{\Omega_{kl}\, \mathbf{a}_l\}_{j_1} & \\ \equiv \sum_{j_2} n_0(j_2) \Big[\sum_{j_1' j_2'} & \big(\Omega_{kl}^{11'}(j_1 j_2, j_1' j_2')\, \mathbf{a}_l(j_1') \\ & + \Omega_{kl}^{12'}(\cdots)\, \mathbf{a}_l(j_2') - \Omega_{kl}^{11}(\cdots)\, \mathbf{a}_l(j_1) \\ & - \Omega_{kl}^{12}(\cdots)\, \mathbf{a}_l(j_2)\big)\Big]\,.\end{aligned} \tag{1.21}$$

The separation into gain and loss collision terms is obvious in Eq. (1.21). The collision integrals appearing in Eq. (1.21) are independent of the particle number density and given by

$$\Omega_{kl}^{11'}(j_1 j_2, j_1' j_2') = -\frac{1}{5 n_0{}^2} \iint \mathrm{d}^3c_1\, \mathrm{d}^3c_2\, f_0(c_1)\, f_0(c_2)\, (g_{j_1}\, g_{j_2})^{-1} \times \int g'\, \mathrm{d}^2e'\, \mathrm{tr}_{j_1}\, \mathrm{tr}_{j_2} [\boldsymbol{\Phi}_k^{j_1} : a^{\,1j_2,\, j_1'j_2'}\, \boldsymbol{\Phi}_l^{j_1'}\, a^{\dagger j_1'j_2',\, j_1 j_2}]\,. \tag{1.22}$$

For $\Omega_{kl}^{12'}$, merely $\boldsymbol{\Phi}_l^{j_1'}$ has to be replaced by $\boldsymbol{\Phi}_l^{j_2'}$. Similarly one has

$$\Omega_{kl}^{11}(j_1 j_2, j_1' j_2') = -\frac{1}{5 n_0{}^2} \iint \mathrm{d}^3c_1\, \mathrm{d}^3c_2\, f_0(c_1)\, f_0(c_2)\, (g_{j_1}\, g_{j_2})^{-1} \times \int g'\, \mathrm{d}^2e'\, \mathrm{tr}_{j_1}\, \mathrm{tr}_{j_2} [\boldsymbol{\Phi}_k^{j_1} : \boldsymbol{\Phi}_l^{j_1}\, a^{j_1 j_2,\, j_1'j_2'}\, a^{\dagger j_1'j_2',\, j_1 j_2}]\,. \tag{1.23}$$

For Ω_{kl}^{12}, $\boldsymbol{\Phi}_l^{j_1}$ has to be replaced by $\boldsymbol{\Phi}_l^{j_2}$.

From (1.22), (1.23) it can be seen that for a purely spherical potential the collision integrals $\Omega_{\eta\mathrm{T}}$, $\Omega_{\mathrm{T}\eta}$ vanish since $\mathrm{tr}\, \boldsymbol{\Phi}_{\mathrm{T}} \equiv 0$. In this case Ω_η does not depend on the j-quantum numbers. Thus, in this "spherical approximation", each of the $\mathbf{a}_\eta(j)$ obeys the same equation independent of j and can then be taken to be equal for all j's (not true for $\mathbf{a}_{\mathrm{T}}(j)$!). The spherical approximation in Eq. (1.19) works if the nonspherical part of the interatomic potential is small compared with the spherical part (which is assumed to be fulfilled here). Then the Eqs. (1.19), (1.20) reduce in the stationary state for a j-independent $\mathbf{a}_\eta$ to

$$\Omega_\eta^{(\mathrm{sph})}\, \mathbf{a}_\eta + \sqrt{2}\, \overline{\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}} = 0\,, \tag{1.24}$$

$$\{\Omega_{\mathrm{T}}\,\mathbf{a}_{\mathrm{T}}\}_{j_1} + \Omega_{\mathrm{T}\eta}(j_1)\,\mathbf{a}_\eta = 0\,, \tag{1.25}$$

where

$$\Omega_{\mathrm{T}\eta}(j_1) = \sum_{j_2 j_1' j_2'} n_0(j_2)\,[\Omega^{11'}_{\mathrm{T}\eta}(j_1\,j_2, j_1'\,j_2') + \Omega^{12'}_{\mathrm{T}\eta}(\cdots) - \Omega^{11}_{\mathrm{T}\eta}(\cdots) - \Omega^{(12)}_{\mathrm{T}\eta}(\cdots)]\,. \tag{1.26}$$

The Eq. (1.25) provides as many coupled linear equations for the $\mathbf{a}_{\mathrm{T}}(j)$ as j values are present. They can easily be solved in order to obtain the tensor polarization of the respective j-subset.

If we consider as a special case the two level system $j = 1/2$, $3/2$ (fine structure dublett in B, Al, Ga) we have

$$\mathbf{a}_{\mathrm{T}}(j = 1/2) \equiv 0, \qquad \mathbf{a}_{\mathrm{T}}(j = 3/2) = \sqrt{\tfrac{3}{2}}\,\langle\overline{\boldsymbol{J}\,\boldsymbol{J}}\rangle_{j=3/2}\,. \tag{1.27}$$

The tensor polarization of the $j = 3/2$ atoms is, according to (1.25), given by

$$\begin{aligned}\langle\overline{\boldsymbol{J}\,\boldsymbol{J}}\rangle_{j=3/2} = &- \bar{\mathrm{p}}\,\frac{\sqrt{3}}{2\,p_0}\,\Omega_{\mathrm{T}\eta}\left(\frac{3}{2}\right)[\sum_{j_2} n_0(j_2)\,(\sum_{j_2'} \Omega^{11'}_{\mathrm{T}}(\tfrac{3}{2}\,j_2, \tfrac{3}{2}\,j_2')\\ &+ \sum_{j_1'} \Omega^{12'}_{\mathrm{T}}(\tfrac{3}{2}\,j_2, j_1'\,\tfrac{3}{2}) - \sum_{j_1' j_2'} \Omega^{11}_{\mathrm{T}}(\tfrac{3}{2}\,j_2, j_1'\,j_2')) - \sum_{j_1' j_2'} n_0(\tfrac{3}{2})\,\Omega^{12}_{\mathrm{T}}(\tfrac{3}{2}\,\tfrac{3}{2}, j_1'\,j_2')]^{-1}\,.\end{aligned} \tag{1.28}$$

The connection with the occupation numbers $N(m)$ can easily be obtained from Eq. (1.15):

$$\boldsymbol{h}\cdot\langle\overline{\boldsymbol{J}\,\boldsymbol{J}}\rangle_{3/2}\cdot\boldsymbol{h} = \frac{N(3/2) + N(-3/2) - N(1/2) - N(-1/2)}{N(3/2) + N(-3/2) + N(1/2) + N(-1/2)}\,. \tag{1.29}$$

Equation (1.28) can be simplified considerably if special assumptions are made for binary scattering amplitude matrix.

II. Interaction Potential, Scattering Amplitude and Cross Sections for ²P-Atoms

1. Interaction Potential

The simplest atoms for which a collisional alignment can be expected are the ^{2}P-atoms in the first excited state with $j = 3/2$ (fine structure splitting). For the nonspherical interaction potential between ^{2}P-atoms the following simple ansatz (which is in accordance with rotational and parity invariance) is made:

$$\begin{aligned}&V(\boldsymbol{x}, \boldsymbol{L}, \boldsymbol{S})\\ &\quad= V_0(r) + V_1(r)[\overline{\boldsymbol{L}_1\boldsymbol{L}_1} + \overline{\boldsymbol{L}_2\boldsymbol{L}_2}] : \hat{\boldsymbol{x}}\,\hat{\boldsymbol{x}} + V_{\mathrm{d,\,d}}\,.\end{aligned} \tag{2.1}$$

In Eq. (2.1), $\boldsymbol{x} = r\,\hat{\boldsymbol{x}}$ is the vector connecting the centers of mass of both atoms, $\boldsymbol{L}$ is the operator of the electronic orbital angular momentum ($L = 1$) and $\boldsymbol{S}$ is the total electron spin operator ($S = 1/2$). The potential functions $V_0(r)$ and $V_1(r)$ can be taken as Lennard-Jones or exponential-inverse sixth power functions; in most cases $V_1 \ll V_0$. Unfortunately, very little is known about the potential parameters for ^{2}P-atoms. The second term of the r.h.s. of Eq. (2.1) is associated with the nonspherical electron distribution. If the angle between the axis of quantization for the angular momentum and the unit vector $\hat{\boldsymbol{x}}$ is denoted by Θ, this term represents a $P_2(\cos\Theta)$-dependence. The third term in Eq. (2.1), $V_{\mathrm{d,\,d}}$ is the magnetic dipole-dipole interaction

$$V_{\mathrm{d,\,d}}(\boldsymbol{x}, \boldsymbol{L}, \boldsymbol{S}) = -\,3\,r^{-3}\,\overline{\boldsymbol{\mu}_1\boldsymbol{\mu}_2} : \hat{\boldsymbol{x}}\,\hat{\boldsymbol{x}}\,, \tag{2.2}$$

where $\boldsymbol{\mu} = \mu_{\mathrm{B}}(g_{\mathrm{L}}\boldsymbol{L} + g_{\mathrm{S}}\boldsymbol{S})$ is the operator of the magnetic moment.

2. Scattering Amplitude in Born Approximation

For temperatures high enough (which are necessary for a high enough population of the $j = 3/2$ level; for Ga, $T > 1500$ K) the first Born approximation may be used to calculate the scattering amplitude from the potential Equation (2.1). Although this approximation is some what questionable for the spherical part it should work for the nonspherical part which is assumed to be small. It will be shown in the following that the collisional alignment is determined solely by the nonspherical part of the potential within the Born approximation. The single channel scattering amplitude matrix describing the transitions between eigenstates of the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ can be written as

$$a^{j_1 j_2,\, j_1' j_2'}_{m_1 m_2,\, m_1' m_2'}(\boldsymbol{k}, \boldsymbol{k}') = -\,\frac{m_{12}}{2\pi\,\hbar^2}\,\langle\boldsymbol{k}, j\,m\,|\,V\,|\,j'\,m', \boldsymbol{k}'\rangle\,, \tag{2.3}$$

where $|\boldsymbol{k}\rangle$ represents a plane wave state ($\langle \boldsymbol{x}|\boldsymbol{k}\rangle \equiv \exp\{i\,\boldsymbol{k}\cdot\boldsymbol{x}\}$) and the state

$$|j\,m\rangle \equiv |j\,m\,L\,S\rangle = \sum_{m_L m_S} (L\,m_{\mathrm{L}}, S\,m_{\mathrm{S}}|j\,m)\,|L\,m_{\mathrm{L}}\rangle\,|S\,m_{\mathrm{S}}\rangle \tag{2.4}$$

is an eigenstate of J^2, J_z, L^2, S^2. In operator form (with respect to magnetic quantum numbers), Eq. (2.3) can be rewritten as

$$a^{j_1 j_2, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}') = -\frac{m_{12}}{2\pi\hbar^2}\langle \boldsymbol{k}|\,P^{j_1 j_2} V\,P^{j_1' j_2'}\,|\boldsymbol{k}'\rangle\,, \tag{2.5}$$

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where

$$P^{j_1 j_2} = P^{j_1}\,P^{j_2}, \tag{2.6a}$$

and

$$P^{j} = \sum_{m} |j\,m\rangle\langle j\,m| \tag{2.6b}$$

is a projection operator into the j-subspace. In Eqs. (2.3), (2.5), m_{12} is the reduced mass and, on the energy shell, the wave numbers k and k' are connected by

$$\hbar^2 k^2/2m_{12} + E(j_1) + E(j_2) = \hbar^2 k'^2/2m_{12} + E(j_1') + E(j_2')\,. \tag{2.7}$$

For the further treatment (evaluation of spin traces occurring in the expressions of cross sections) it is very useful to introduce the Cartesian tensor operators $T^{jj'}_{\mu}$, $T^{jj'}_{\mu\nu}$ defined in Refs. [12, 20] which describe the transitions in j-space. Using some Racah algebra we find

$$P^j L_\mu P^{j'} = A(j, j')\,T^{jj'}_{\mu}\,, \qquad P^j S_\mu P^{j'} = A'(j, j')\,T^{jj'}_{\mu}\,, \qquad P^j\,\overline{L_\mu L_\nu}\,P^{j'} = B(j, j')\,T^{jj'}_{\mu\nu}\,, \tag{2.8}$$

with

$$\begin{aligned} A(j, j') &= \sqrt{2(2j+1)(2j'+1)}\,(-1)^{1/2-j'}\,W(1\,1\,j\,j';1\,\tfrac{1}{2})\,,\\ A'(j, j') &= \tfrac{1}{2}\sqrt{2(2j+1)(2j'+1)}\,(-1)^{j'+1/2}\,W(\tfrac{1}{2}\,\tfrac{1}{2}\,j\,j';1\,1)\,,\\ B(j, j') &= \sqrt{(2j+1)(2j'+1)}\,(-1)^{3/2-j'}\,W(1\,1\,j\,j';2\,\tfrac{1}{2})\,. \end{aligned} \tag{2.9}$$

The $W(\cdots)$ are Racah coefficients which contain the selection rules. Thus one obtains for the magnetic dipole-dipole term

$$P^{j_1 j_2}\,\overline{\boldsymbol{\mu}_1\,\boldsymbol{\mu}_2}\,P^{j_1' j_2'} = \mu_{\mathrm{B}}^2\,C(j_1\,j_2, j_1'\,j_2')\,\boldsymbol{T}^{j_1 j_1'}\,\boldsymbol{T}^{j_2 j_2'}\,, \tag{2.10a}$$

with

$$\begin{aligned} C(j_1\,j_2, j_1'\,j_2') = {} & g_L^2\,A(j_1, j_1')\,A(j_2, j_2') + g_S^2\,A'(j_1, j_1')\,A'(j_2, j_2')\\ & + g_{\mathrm{L}}\,g_{\mathrm{S}}(A(j_1, j_1')\,A'(j_2, j_2') + A(j_2, j_2')\,A'(j_1, j_1'))\,. \end{aligned} \tag{2.10b}$$

For the evaluation of (2.5) also the following matrix elements are needed:

$$-(m_{12}/2\pi\hbar^2)\,\langle \boldsymbol{k}|\,V_0\,|\boldsymbol{k}'\rangle \equiv a_0(q)\,; \qquad -(m_{12}/2\pi\hbar^2)\,\langle \boldsymbol{k}|\,V_1\,\overline{\hat{\boldsymbol{x}}\,\hat{\boldsymbol{x}}}\,|\boldsymbol{k}'\rangle \equiv \overline{\boldsymbol{q}\,\boldsymbol{q}}\,b(q)\,, \tag{2.11}$$

$$\frac{3\,m_{12}\,\mu_{\mathrm{B}}^2}{2\pi\hbar^2}\langle \boldsymbol{k}|\,r^{-3}\,\overline{\hat{\boldsymbol{x}}\,\hat{\boldsymbol{x}}}\,|\boldsymbol{k}'\rangle \equiv \overline{\boldsymbol{q}\,\boldsymbol{q}}\,c_{\mathrm{d,\,d}}(q)\,, \tag{2.12}$$

where $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$ is the momentum transfer and (with $m = 2m_{12}$)

$$a_0(q) = -\frac{m}{\hbar^2 q}\int_{R_0}^{\infty} V^0(r)\sin(q\,r)\,r\,\mathrm{d}r\,, \tag{2.13}$$

$$b(q) = +\frac{m}{\hbar^2 q^4}\int_{R_0}^{\infty} V_1(r)\left[\sin(q\,r)\left(q\,r - \frac{3}{q\,r}\right) + 3\cos(q\,r)\right]\mathrm{d}r\,. \tag{2.14}$$

Notice that for small q values one has

$$b(q) \approx -\frac{m}{15\hbar^2}\left[\int_{R_0}^{\infty} V_1(r)\,r^4\,\mathrm{d}r - \frac{1}{14}\,q^2\int_{R_0}^{\infty} V_1(r)\,r^6\,\mathrm{d}r\right]. \tag{2.14a}$$

(For $c_{\mathrm{d,\,d}}(q)$, V_1 has merely to be replaced by $-3\,\mu_{\mathrm{B}}^2\,r^{-3}$ in (2.14)).

In the Eqs. (2.13), (2.14) a cutoff radius R_0 has been introduced to account for the hard-core like behavior of the repulsive interaction for small distances. Using the Eqs. (2.1), (2.5)—(2.14) we obtain the Born approximation expression for the single channel scattering amplitude matrix:

$$\begin{aligned} a^{j_1 j_2, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}') &= a_0(q)\, P^{j_1 j_2}\, \delta^{j_1 j_1'}\, \delta^{j_2 j_2'} \\ &+ \overline{q_\mu q_\nu} \{ b(q)\, B(j_1, j_1')\, T^{j_1 j_1'}_{\mu\nu}\, P^{j_2}\, \delta^{j_2 j_2'} + (1,2) \text{ interchanged} + c_{\mathrm{d},\mathrm{d}}(q)\, C(j_1 j_2, j_1' j_2')\, T^{j_1 j_1'}_{\mu}\, T^{j_2 j_2'}_{\nu} \}. \end{aligned} \tag{2.15}$$

Simultaneous j-transitions in both atoms are solely caused by the magnetic dipole-dipole interaction.

3. *Orientation and Reorientation Cross Sections*

The scattering amplitude Eq. (2.15) is now used to calculate the molecular orientation and reorientation cross sections for the tensor polarization occurring in the collision integrals Eqs. (1.22), (1.23). Using (2.15) and the trace formulae of Ref. [12] we obtain the orientation cross section tensor (which describes the production of a tensor polarization in a collision) as

$$\begin{aligned} &\mathrm{tr}_1\, \mathrm{tr}_2 \{ \boldsymbol{\Phi}^{j_1}_{\mathrm{T}}\, a^{j_1 j_2, j_1' j_2'}\, a^{\dagger j_1' j_2', j_1 j_2} \} \\ &= \overline{\boldsymbol{q}\boldsymbol{q}} \Big\{ g_{j_2} \sqrt{g_{j_1}} \delta_{j_2 j_2} \Big[2 a_0(q)\, b(q)\, B(j_1, j_1')\, \delta_{j_1 j_1'} - \frac{10}{3} \sqrt{\frac{3}{7}}\, q^2 b^2(q)\, B^2(j_1, j_1') \\ &\quad \times (-1)^{j_1 - j_1'}\, W(j_1 j_1 2\, 2; 2 j_1') \Big] + q^2 c^2_{d,d}(q)\, C^2(j_1 j_2, j_1' j_2') (-1)^{j_1 - j_1'} W(j_1 j_1 1\, 1; 2 j_1') \Big\}. \end{aligned} \tag{2.16}$$

Note that $j_1 = 3/2$ and that for $j_1 = j_1' = 3/2$ the second term of the r.h.s. of (2.16) vanishes since the corresponding Racah coefficient is zero. Clearly, the "orientation cross section tensor" (2.16) vanishes for a purely spherical interaction. Since one has $\boldsymbol{q} = (m_{12}/\hbar)\,(g\,\boldsymbol{e} - g'\,\boldsymbol{e}')$, the elastic part of (2.16) is a tensor symmetric in $\boldsymbol{e}$ and $\boldsymbol{e}'$.

Similarly, the reorientation cross section determining $\Omega^{11'}_{\mathrm{T}}$ is:

$$\begin{aligned} &\mathrm{tr}_1\, \mathrm{tr}_2 \{ \boldsymbol{\Phi}^{j_1}_{\mathrm{T}} \colon a^{j_1 j_2, j_1' j_2'}\, \boldsymbol{\Phi}^{j_1'}_{\mathrm{T}}\, a^{\dagger j_1' j_2', j_1 j_2} \} \\ &= 5 q^4 g_{j_2}\, \delta_{j_1 j_1'} \{ q^{-4} a_0^2(q)\, g_{j_1}\, \delta_{j_2 j_2'} + \tfrac{2}{3} b^2(q)\, B^2(j_1, j_1)\, W(j_1 j_1 j_1 j_1; 2\, 2)\, g_{j_1}\, \delta_{j_2 j_2'} \\ &\quad + \tfrac{2}{3} b^2(q)\, g^{-1}_{j_2}\, B^2(j_2, j_2')\, g_{j_1} - \tfrac{2}{3} c^2_{d,d}(q)\, g^{-1}_{j_2}\, C^2(j_1 j_2, j_1 j_2')\, W(j_1 j_1 j_1 j_1; 1\, 2) \}. \end{aligned} \tag{2.17}$$

In (2.17), $j_1 = j_1' = 3/2$ gives the only nonzero contribution. The reorientation cross section determining Ω^{11}_{T} is given by

$$\begin{aligned} &\mathrm{tr}_1\, \mathrm{tr}_2 \{ \boldsymbol{\Phi}^{j_1}_{\mathrm{T}} \colon \boldsymbol{\Phi}^{j_1}_{\mathrm{T}}\, a^{j_1 j_2, j_1' j_2'}\, a^{\dagger j_1' j_2', j_1 j_2} \} \\ &= 5 q^4 g_{j_2} \{ q^{-4} a_0^2(q)\, g_{j_1}\, \delta_{j_1 j_1'}\, \delta_{j_2 j_2'} + \tfrac{2}{3} b^2(q)\, B^2(j_1, j_1')\, \delta_{j_2 j_2'} + \tfrac{2}{3} b^2(q)\, B^2(j_2, j_2')\, g_{j_1} g^{-1}_{j_2}\, \delta_{j_1 j_1'} \\ &\quad + \tfrac{2}{3} c^2_{\mathrm{d},\mathrm{d}}(q)\, C^2(j_1 j_2, j_1' j_2') \}. \end{aligned} \tag{2.18}$$

Here, $j_1 = 3/2$, but j_1' can take the values 1/2, 3/2.

The reorientation cross section occurring in the expressions for $\Omega^{12'}_{\mathrm{T}}$, Ω^{12}_{T} are

$$\begin{aligned} &\mathrm{tr}_1\, \mathrm{tr}_2 \{ \boldsymbol{\Phi}^{j_1}_{\mathrm{T}} \colon a^{j_1 j_2, j_1' j_2'}\, \boldsymbol{\Phi}^{j_2'}_{\mathrm{T}}\, a^{\dagger j_1' j_2', j_1 j_2} \} \\ &= q^4 \sqrt{g_{j_1} g_{j_2}} \{ \tfrac{4}{3} b^2(q)\, B(j_1, j_1)\, B(j_2, j_2)\, \delta_{j_1 j_1'}\, \delta_{j_2 j_2'} + c^2_{\mathrm{d},\mathrm{d}}(q)\, C^2(j_1 j_2, j_1' j_2')\, (-1)^{j_1 + j_2 - j_1' - j_2'} \\ &\quad \times W(j_1 j_1 1\, 1; 2 j_1')\, W(j_2' j_2' 1\, 1; 2 j_2) \}, \end{aligned} \tag{2.19}$$

where $j_1 = j_2' = 3/2$, and

$$\begin{aligned} &\mathrm{tr}_1\, \mathrm{tr}_2 \{ \boldsymbol{\Phi}^{j_1}_{\mathrm{T}} \colon \boldsymbol{\Phi}^{j_2}_{\mathrm{T}}\, a^{j_1 j_2, j_1' j_2'}\, a^{\dagger j_1' j_2', j_1 j_2} \} \\ &= q^4 \sqrt{g_{j_1} g_{j_2}} \{ \tfrac{4}{3} b^2(q)\, B(j_1, j_1)\, B(j_2, j_2)\, \delta_{j_1 j_1'}\, \delta_{j_2 j_2'} + c^2_{\mathrm{d},\mathrm{d}}(q)\, C^2(j_1 j_2, j_1' j_2') (-1)^{j_1 + j_2 - j_1' - j_2'} \\ &\quad \times W(j_1 j_1 1\, 1; 2 j_1')\, W(j_2 j_2 1\, 1; 2 j_2') \}, \end{aligned} \tag{2.20}$$

where $j_1 = j_2 = 3/2$.

If the contribution of the magnetic dipole-dipole term in the nonspherical interaction (2.1) is small compared with the other terms then the terms proportional to $c_{\mathrm{d,d}}^2$ can be neglected in the cross sections (2.16)—(2.20). In tis case the following simplifications are achieved:

$$\Omega_{\mathrm{T}}^{12'}(j_1 j_2, j_1' j_2') = \Omega_{\mathrm{T}}^{12}(j_1 j_2, j_1' j_2') = \Omega_{\mathrm{T}}^{12}(j_1 j_2)\, \delta_{j_1 j_1'}\, \delta_{j_2 j_2'}\,, \tag{2.21}$$

$$\Omega_{\mathrm{T}\eta}(j_1 j_2, j_1' j_2') = \Omega_{\mathrm{T}\eta}(j_1 j_1')\, \delta_{j_2 j_2'}\,, \tag{2.22}$$

and

$$\Omega_{\mathrm{T}}^{11}(j_1 j_2, j_1' j_2') - \Omega_{\mathrm{T}}^{11'}(j_1 j_2, j_1' j_2') = (\Omega_{\mathrm{T}}^{11}(j_1 j_1') - \Omega_{\mathrm{T}}^{11'}(j_1 j_1'))\, \delta_{j_2 j_2'}\,. \tag{2.23}$$

The Eqs. (2.21) to (2.23) are very useful for a calculation of the collision integrals since, e.g., the j_2- and j_2'-summations can then easily be performed.

Next, it is demonstrated (for Ga atoms at 1600 K as example) that the magnetic dipole-dipole interaction is indeed negligible. At 1600 K, the thermal momentum transfer (for a representative scattering angle of 90°), $\bar{q} = \sqrt{2 m k_{\mathrm{B}} T / \hbar^2}$ is of the order of 10^2 Å^{-1}. Since the cutoff radius R_0 (hard sphere diameter) is of the order 1 Å the dimensionless quantity $\bar{q} \cdot R_0$ is of the order of 10^2. For an order of magnitude consideration the integral defining $c_{\mathrm{d,d}}$ is roughly estimated by replacing $\sin(q R_0)$, $\cos(q R_0)$ by unity and by neglecting terms proportional to $(q R_0)^{-1}$ compared with unity (the angular momentum coefficients are also of order unity). Then one finds

$$\bar{\sigma}_{\mathrm{d,d}} \sim 10^{-1} (m \mu_{\mathrm{B}}^2 / \hbar^2)^2 (\bar{q} \cdot R_0)^{-2}\,. \tag{2.24}$$

Since $(m \mu_{\mathrm{B}}^2/\hbar^2)$ is of the order 1 Å, $\bar{\sigma}_{\mathrm{d,d}}$ is of the order 10^{-3} Å^2. This is a very small value compared with reorientation cross sections due to the nonspherical electron distribution obtained from collisional broadening of spectral lines[21] which are of the order of 10 Å^2. Furthermore, this is supported by the fact that the effective reorientation cross section is of order Å^2 at room temperature[22, 23] even for a molecule with very small nonsphericity of the interaction like HD. For ^{2}P atoms the orientation and reorientation cross sections can be expected to be at least of the same order of magnitude. Thus the magnetic dipole-dipole contribution to those cross sections can surely be neglected.

III. Theoretical Results and Experimental Aspects

1. Collision Integrals and Effective Cross Sections

Using Eqs. (1.22), (1.23), (1.26) and (2.16) to (2.22), we evaluate now the collision brackets $\Omega_{\mathrm{T}\eta}$, $\Omega_{\mathrm{T}}^{11'}$, Ω_{T}^{11}. It can be seen from Eq. (1.28) after some rearrangement that Ω_{T}^{12} and $\Omega_{\mathrm{T}}^{12'}$ cancel [because of Eq. (2.21)] and $\Omega_{\mathrm{T}}^{11'}$, Ω_{T}^{11} occur only in the combination as in Equation (2.23). For further calculations some kinematic relations are needed. It is useful to introduce dimensionless relative velocity variables

$$\boldsymbol{\gamma} = \gamma\, \boldsymbol{e} = \tfrac{1}{2} \sqrt{m/k_{\mathrm{B}} T_0}\, \boldsymbol{g}\,,$$
$$\boldsymbol{\gamma}' = \gamma'\, \boldsymbol{e}' = \tfrac{1}{2} \sqrt{m/k_{\mathrm{B}} T_0}\, \boldsymbol{g}'\,. \tag{3.1}$$

With (3.1) one has

$$f_0(c_1)\, f_0(c_2)\, \mathrm{d}^3 c_1\, \mathrm{d}^3 c_2 = n_0{}^2 \pi^{-3} \exp(-V_{\mathrm{S}}{}^2) \exp(-\gamma^2)\, \gamma^2\, \mathrm{d}^3 V_{\mathrm{S}}\, \mathrm{d}^2 e\, \mathrm{d}\gamma, \tag{3.2}$$

where $\boldsymbol{V}_{\mathrm{S}}$ is the dimensionless center of mass velocity. The momentum transfer in a collision can be expressed by

$$\hbar\, \boldsymbol{q} = \sqrt{m k_{\mathrm{B}} T_0}\, (\gamma\, \boldsymbol{e} - \gamma'\, \boldsymbol{e}')\,. \tag{3.3}$$

Here γ' is, according to the conservation of energy determined by

$$\gamma'^2 = \gamma^2 + \Delta E / k_{\mathrm{B}} T_0\,;$$
$$\Delta E = E(j_1) + E(j_2) - E(j_1') - E(j_2')\,. \tag{3.4}$$

Thus q depends on γ, j_1, j_2, j_1', j_2' and on the angle of deflection $\vartheta = \arccos(\boldsymbol{e} \cdot \boldsymbol{e}')$.

In the expression Eq. (1.26) for $\Omega_{\mathrm{T}\eta}$ ($j_1 = 3/2$) the tensor

$$\Delta \boldsymbol{\Phi}_\eta = \boldsymbol{\Phi}_\eta(\boldsymbol{c}_1) + \boldsymbol{\Phi}_\eta(\boldsymbol{c}_2) - \boldsymbol{\Phi}_\eta(\boldsymbol{c}_1') - \boldsymbol{\Phi}_\eta(\boldsymbol{c}_2')$$

appears. It can be written as

$$\Delta \boldsymbol{\Phi}_\eta = \sqrt{2}\, [\gamma^2\, \overline{\boldsymbol{e}\, \boldsymbol{e}} - \gamma'^2\, \overline{\boldsymbol{e}'\, \boldsymbol{e}'}]\,. \tag{3.5}$$

Using Eqs. (3.3) to (3.5) we obtain

$$\overline{\boldsymbol{q}\, \boldsymbol{q}} : \Delta \boldsymbol{\Phi}_\eta = -\frac{2\sqrt{2}}{3}\, q^2\, \Delta E / k_{\mathrm{B}} T_0\,. \tag{3.6}$$

Since ΔE ($= E(j_1 = 3/2) - E(j_1 = 1/2)$ here, i.e. equal to the fine structure splitting) is zero for energetically elastic collisions and since in $\Omega_{\mathrm{T}\eta}$ (3.6) appears as a factor, the collision integral $\Omega_{\mathrm{T}\eta}$

vanishes unless inelastic collisions occur. According to Eq. (1.28) also the collisional alignment is zero in Born approximation if only elastic collisions occur. This statement remains true even for the distorted wave Born approximation. This is the reason why "uncoupled" elastic model of Coope and Snider[16] is useless for our case.

The collision integrals are proportional to the total particle number density n_0. It is therefore useful to factorize them in the following way ($\sigma_{..}$ are effective cross sections depending only on T_0)

$$\Omega_{..} = n_0\, v_0\, \sigma_{..}\,, \tag{3.7}$$

where $v_0 = 4\sqrt{k_{\rm B} T_0 / m\pi}$ is a thermal velocity. With the definition for $\Omega_{\rm T}$ through

$$\{\Omega_{\rm T}\, \mathbf{a}_{\rm T}\}_{3/2} \equiv \Omega_{\rm T}\,(3/2)\; \mathbf{a}_{\rm T}\,(3/2) \tag{3.8}$$

and by use of Eqs. (1.22), 1.23), (1.26), (1.28), (2.16), to (2.23) and (3.1) to (3.7) and tabulated values of the Racah coefficients[24] one obtains the following effective cross sections for ^{2}P-atoms with $j = 1/2$, $j = 3/2$.

Effective coupling cross section:

$$\sigma_{{\rm T}\eta} = \frac{32\pi}{45\sqrt{3}}\,\frac{\Delta E}{k_{\rm B} T_0} \int\!\!\int \exp\{-\gamma^2\}\, \gamma^2\, \gamma'\, b^2(q_{\rm inel})\, q_{\rm inel}^4 \sin\vartheta \,{\rm d}\vartheta\, {\rm d}\gamma\,, \tag{3.9}$$

[$q_{\rm inel} = q(\gamma, \gamma', \vartheta)$ after Equations (3.3), 3.4)].

Effective relaxation cross sections:

$$\sigma_{\rm T,inel} = \frac{5\sqrt{3}}{2} \left(\frac{\Delta E}{k_{\rm B} T_0}\right)^{-1} \sigma_{{\rm T}\eta}\,, \tag{3.10}$$

$$\sigma_{\rm T,el} = \frac{32\pi}{45} \int\!\!\int \exp\{-\gamma^2\}\, \gamma^3\, b^2(q_{\rm el})\, q_{\rm el}^4 \sin\vartheta \,{\rm d}\vartheta\, {\rm d}\gamma. \tag{3.11}$$

The subscript "inel" refers to the $1/2 \rightarrow 3/2$ collisions while the subscript "el" refers to the elastic $3/2 \rightarrow 3/2$ collisions. Also the effective coupling cross section is positive because of the remarkable identity Eq. (3.10) which is valid in Born approximation.

2. *Flow Induced Tensor Polarization*

Insertion of the cross sections (3.9)—(3.11) into Eq. (1.28) yields the following expression for the tensor polarization of the $j = 3/2$ atoms caused by the friction pressure tensor $\bar{\mathfrak{p}}$:

$$\langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle_{j=3/2} = -\frac{1}{\sqrt{2}}\, \frac{1}{p_0}\, \frac{\Delta E}{k_{\rm B} T_0}\, (5 + 2\,\sigma_{\rm T,el}/\sigma_{\rm T,inel})^{-1}\, \bar{\mathfrak{p}}\,. \tag{3.12}$$

The alignment is directly proportional to the dimensionless fine structure energy splitting. The connection (1.24) between the friction pressure tensor $\bar{\mathfrak{p}}$ and the velocity gradient tensor is, in spherical approximation, given by the well known relation

$$\bar{\mathfrak{p}} = -2\eta\, \frac{\overline{\partial \boldsymbol{v}}}{\partial \boldsymbol{x}}\,; \quad \eta = p_0/\Omega_\eta^{\rm (sph)}\,,\; \Omega_\eta^{\rm (sph)} = n_0\, v_0\, \sigma_\eta^{\rm (sph)} \tag{3.13}$$

where $\Omega_\eta^{\rm (sph)}$ can be expressed in terms of a Chapman-Cowling integral: $\Omega_\eta^{\rm (sph)} = \frac{8}{5}\, n_0\, \Omega^{(2,2)}$. Since Ω_η is proportional to the equilibrium pressure p_0, the viscosity η is pressure independent. Thus the tensor polarization (3.12) is inversely proportional to the pressure p_0.

The temperature dependence of the alignment can be estimated as follows: Inserting (3.13) into (3.12) we see that the temperature behavior is determined by the temperature dependence of

$$[p_0(T_0)\, v_0\, \sigma_\eta(T_0)\, (5 + 2\,\sigma_{\rm T,el}\,(T_0)/\sigma_{\rm T,inel}(T_0)]^{-1}\,.$$

The ratio of elastic and inelastic effective relaxation cross sections (in the following abbreviated with β) can be assumed to be only weakly temperature dependent. For the high temperatures considered the cross section $\sigma_\eta(T_0)$ is practically constant (hard spheres). Since $v_0 \sim \sqrt{T_0}$, thete mperature dependence of (3.12) is in good approximation determined by that of $(p_0(T_0)\sqrt{T_0})^{-1}$. Since in any case p_0 increases with temperature the alignment will decrease with increasing temperature. For experiments performed such that $p_0(T_0)$ is the phase coexistence pressure one has a strong temperature dependence of the effect. This is in qualitative agreement with Toschek's results.

Next, an estimate is given for the magnitude of the tensor polarization, i.e. the quantity

$$\boldsymbol{h} \cdot \langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle \cdot \boldsymbol{h} \equiv \langle \overline{\boldsymbol{J}_z\, \boldsymbol{J}_z} \rangle\,.$$

As an example, Ga atoms at 1600 K will be considered. For this temperature about 50% will be in the first excited state $j = 3/2$. The pressure p_0 shall be 1 torr which corresponds to the steam pressure at this temperature. (For smaller pressures, the mean free path becomes comparable with the dimensions of the vessel and Knudsen effects will be important). The magnitude G of the velocity gradient is introduced by

$$G = \boldsymbol{h} \cdot \frac{\overline{\partial \boldsymbol{v}}}{\partial \boldsymbol{x}} \cdot \boldsymbol{h}\,.$$

With $\Delta E = 0.1$ eV, $v_0 \sim 10^5$ cm sec^{-1} and $\sigma_\eta \sim 20$ Å^2 (taken from a gas kinetic diameter of 3 Å) one obtains

$$\langle \overline{J_z J_z} \rangle \sim 2 \cdot 10^{-7} G (1 + \tfrac{2}{5} \beta)^{-1} . \tag{3.14a}$$

In a laminar flow between rotating cylinders G-values up to $5 \cdot 10^2$ sec^{-1} are accessible. Thus one has

$$\langle \overline{J_z J_z} \rangle_{\max} \sim 10^{-4} (1 + \tfrac{2}{5} \beta)^{-1} . \tag{3.14b}$$

The ratio β can be expected to be of order unity. Thus the alignment will be of order 10^{-4} for a Couette flow arrangement. For much larger gradients as they may occur in effusive flow an alignment of the order of 10^{-2} can be expected. In the latter case it could be detected in a Stern-Gerlach apparatus. Much smaller alignments are detectable with optical methods, e.g. flow birefringence[2].

3. *Flow Birefringence*

The connection between flow birefringence and flow induced alignment is discussed in this section. Flow birefringence occurs if the dielectric tensor $\boldsymbol{\epsilon}$ possesses an irreducible part. For dilute gases one has the relation[1]

$$\boldsymbol{\epsilon} = \boldsymbol{\delta} + 4 \pi n_0 \langle \boldsymbol{\alpha} \rangle , \tag{3.15}$$

where $\boldsymbol{\alpha}$ is the tensor of the atomic polarizability and $\langle \cdots \rangle$ refers to an average over the one particle distribution. The tensor $\boldsymbol{\alpha}$ can be written as

$$\boldsymbol{\alpha} = \alpha \, \boldsymbol{\delta} + \alpha' \, \overline{\boldsymbol{L} \boldsymbol{L}} . \tag{3.16}$$

Since only the $j = 3/2$ atoms give contributions to $\langle \overline{\boldsymbol{L} \boldsymbol{L}} \rangle$ one finds

$$\langle \overline{\boldsymbol{L} \boldsymbol{L}} \rangle = \tfrac{1}{3} \, p(\tfrac{3}{2}) \, \langle \overline{\boldsymbol{J} \boldsymbol{J}} \rangle_{j=3/2} . \tag{3.17}$$

The occupation probability of the $j = 3/2$ state is given by

$$p(3/2) \tag{3.18}$$

$$= 2 \exp\{- \Delta E / k_{\mathrm{B}} T_0\} / (1 + 2 \exp\{- \Delta E / k_{\mathrm{B}} T_0\} .$$

Using Eqs. (3.15) — (3.18) we obtain the irreducible part of the electric permeability tensor as

$$\overline{\boldsymbol{\epsilon}} = (2 \pi / 3) \, n_0 (j = 3/2) \, \alpha' \langle \overline{\boldsymbol{J} \boldsymbol{J}} \rangle_{j=3/2} . \tag{3.19}$$

It is proportional to the magnitude of the tensor polarization and to the number density of atoms in the excited state. The relative change of the index of refraction[1], $\delta \nu$, (with respect to $\boldsymbol{E}$-vectors parallel to the two respective major axes of the velocity gradient tensor which are perpendicular to the direction of light propagation) is then proportional to $\langle \overline{J_e J_e} \rangle$. Here, $\boldsymbol{e}$ is one of those major axes (for the other one only the sign changes in the case of the flow between rotating cylinders). Thus, a measurement of $\delta \nu$ yields also the flow induced alignment if the polarizability α' is known.

4. *Conclusion*

Higher values for the alignment could be achieved with atomic beams emerging from nozzles or from an oven. This is the case in the Toschek experiment. But this experiment is not suitable for a comparison with the above results since the effusion conditions are not known. If, nevertheless, the experimental result (the measured tensor polarization varied between 1% and 10% and decreased with increasing temperature) is compared with Eq. (3.12) one finds that the temperature behavior is reproduced qualitatively in the right way. Furthermore a magnitude

$$\partial v_z / \partial z = G \sim 10^5 \text{ sec}^{-1}$$

$\boldsymbol{e}_z$ is the direction of flow) at the exit of the oven can be estimated from the experimental value of $N(\tfrac{3}{2}) - N(\tfrac{1}{2}) / (N(\tfrac{3}{2}) + N(\tfrac{1}{2}))$. It is assumed thereby that the mean free path of the atoms outside the oven is so large that collisions are negligible and the tensor polarization is practically convectively transported from the oven to the Stern-Gerlach analyzing magnet ($\boldsymbol{H} \perp \boldsymbol{e}_z$).

To summarize shortly, the following statement can be made: A flow field causes a tensorpolarization of atoms by means of collisions if $j \geqq 1$ and the interatomic potential is nonspherical. The alignment will be small for an incompressible viscous flow but detectable with optical methods. It decreases with increasing temperature. It is desirable to perform experiments in order to obtain information on atomic orientation and reorientation cross sections for the total internal angular momentum.

[1] S. Hess, Phys. Letters **30 A**, 239 [1969]; Springer Tracts Mod. Phys. **54**, 136 [1970].; in The Boltzmann Equation – Theory and Applications, eds. E. G. D. Cohen and W. Thirring, Springer-Verlag-Wien 1973.

[2] F. Baas, Phys. Letters **36 A**, 107 [1971].

[3] H. Senftleben, Phys. Z. **31**, 822, 961 [1930].

[4] J. J. M. Beenakker, G. Scoles, H. F. P. Knaap, and R. M. Jonkman, Phys. Letters **2**, 5 (1962).

[5] For a review see J. J. M. Beenakker and F. R. McCourt, Ann. Rev. Phys. Chem. **21**, 136 [1970]; J. J. M. Beenakker, in The Boltzmann Equation – Theory and Applications, E. G. D. Cohen and W. Thirring. Springer-Verlag-Wien 1973.

[6] F. R. McCourt and R. F. Snider, J. Chem. Phys. **46**, 2387 [1967]; **47**, 4117 [1967]. – A. C. Levi and F. R. McCourt, Physica **38**, 415 [1968].

[7] S. Hess and L. Waldmann, Z. Naturforsch. **26 a**, 1057 [1971]. – W. E. Köhler and H. H. Raum, Z. Naturforsch. **27 a**, 1383 [1972].

[8] H. Senftleben, Physik. Z. **32**, 550 [1931]. – D. Stichtig, Ann. Physik **38**, 274 [1940].

[9] L. Waldmann and H. D. Kupatt, Z. Naturforsch. **18 a**, 86 [1963]; S. Hess, Diplomarbeit, Erlangen 1964.

[10] S. Hess and L. Waldmann, Z. Naturforsch. **21 a**, 1529 [1966].

[11] L. J. F. Hermans, A. Schutte, H. F. Knaap, and J. J. M. Beenakker, Physica **51**, 319 [1971].

[12] W. E. Köhler, S. Hess, and L. Waldmann, Z. Naturforsch. **25 a**, 336 [1970].

[13] P. Toschek, Z. Physik **187**, 56 [1965].

[14] L. Waldmann, Z. Naturforsch. **12 a**, 660 [1957]; **13 a**, 609 [1958].

[15] R. F. Snider, J. Chem. Phys. **32**, 1051 [1960].

[16] J. A. R. Coope and R. F. Snider, J. Chem. Phys. **56**, 2049 [1972].

[17] H. Grad, Comm. Pure Appl. Math. **2**, 331 [1949]. – L. Waldmann, Z. Naturforsch. **18 a**, 1033 [1963].

[18] H. H. Raum and W. E. Köhler, Z. Naturforsch. **25 a**, 1178 [1970].

[19] J. P. Toennies, Z. Physik **182**, 257 [1965].

[20] S. Hess, Z. Naturforsch. **24 a**, 1675 [1969].

[21] D. W. Cook, R. S. Timsit, and A. D. May, Can. J. Phys. **47**, 747 (1969).

[22] W. E. Köhler, Z. Naturforsch. **26 a**, 1926 [1971].

[23] H. Hulsman, E. van Waasdijk, A. L. Burgmans, H. F. P. Knaap, and J. J. Beenakker, Physica **50**, 33 [1970].

[24] Tables of Racah Coefficients, ed. T. Ishidzu, Pan-Pacific Press, Tokyo 1960.