this method of selectively influencing the molecules and its practical application.

It is, however, important to remember the secondary chemical processes which may reduce the selectivity. Complex molecules usually decay into radicals from electronically excited states. It is, therefore, important to select molecules whose decay products have no appreciable effect on the isomerization reaction, or have low decay probability. The following excitation scheme can be used for such experiments. The molecule is first taken to the low-lying vibrational levels of the singlet electronic state and then undergoes transitions to the triplet state, followed by relaxation to the ground state. Molecular isomerization will be the leading process in this scheme.

Apart from its selective effect, multistep excitation of molecules can also be used in other fields, for example, in the spectroscopy of electronically excited states of complex isolated molecules.

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Anomalous Senftleben effect

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Some features of the Senftleben effect are considered for polar molecules. It is shown that, in contrast to the Kagan vector, the use of the Waldmann vector, previously employed in the description of nonspherical collisions in polar gases, is unjustified. It is established that molecular collisions leading to the violation of the principle of detailed balancing are accompanied by a change in the component of the angular momentum along the axis of symmetry of the molecule. The characteristic collision frequencies associated with the nonequilibrium polarization of the angular momenta of the molecules are determined for the CH_3CN gas.

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1. INTRODUCTION

Studies of phenomena such as the change in the transport coefficients in external fields, birefringence in a viscous flow of gas, the thermomagnetic rotation effect, depolarized Rayleigh scattering, NMR and ESR relaxation, and so on,[1] have resulted in an increased interest in the properties of nonspherical scattering by monatomic molecules. The principal aim of such investigations is to obtain information on the frequencies of elastic and inelastic collisions involving a change in the direction of the angular momentum of the molecule. This information is essential for the solution of many applied problems and, in particular, problems such as the development of masers using rotational transitions in molecules and controlled chemical reactions.

The common feature of all the phenomena mentioned above is the polarization of the angular momenta in a gas of monatomic molecules when macroscopic-temperature gradients or velocity gradients are established. The existence of this polarization is directly confirmed by the appearance of birefringence in a viscous gas flow[2] and also the polarization of molecules in the gas stream issuing from an ultrasonic nozzle.[3] An external field acting on the dipole or magnetic moment of the molecules changes the polarization of the angular momenta and this, in turn, produces a change in the transport coefficients of the gas (this is the Senftleben effect).

Experiment shows that the resulting polarization of the angular momenta is connected with the point symmetry of the gas molecules. Thus, for simple diatomic and linear molecules, and molecules in the form of a spherical spinning top, which exhibit high symmetry, the change in the polarization in the field leads to a reduction in thermal conductivity and viscosity in a low-pressure gas of such molecules. However, in highly polar gases (CH_3CN, C_2H_5CN, CH_3NO_2, etc.), the dependence of the heat flow on the applied field is anomalous: the application of a low electric field results in an increase rather than a reduction in the heat flow.[4-6] It has been shown[7-9] that, if there are collision for which the probabilities of direct and inverse collisions are not equal, this may result in an increase in the transport coefficients in the field. However, existing theory does not provide an explanation of the anisotropic effect, i.e., the dependence of the phenomenon on the angle between the field and the temperature gradient, and the connection between the phenomenon and the point symmetry of the gas molecules.

The usual Senftleben effect is due to collisions resulting in a change in the direction of the angular momentum of the molecule. The frequency of such collisions is usually obtained from the field dependence of the transport coefficients.[10] The case of highly polar molecules, for which the anomalous Senftleben effect is observed, is different in that it involves inelastic collisions in which there is a change in the angular momentum component along the rotational axis of the molecule. The contribution of such collisions increases as the shape of the molecule departs from the spherical shape.

To investigate the polarization of angular momenta in a nonequilibrium state, we shall employ the model based on nonspherical potential scattering which has been used [11,12] to study the scattering of diatomic molecules and [13] the scattering of molecules with arbitrary symmetry. Since the mean wavelength of the molecules in the gas is small even in comparison with the molecular ineraction range and, moreover, with the exception of light gases such as H_2, D_2, and HD, the rotational levels excited at room temperature have quantum numbers that are large in comparison with unity, we shall use the quasiclassical approximation both for the translational and the rotational degrees of freedom. The transport equation for a gas consisting of monatomic molecules with rotational degrees of freedom was obtained in this approximation by Borman *et al.*[14] They showed that, in the quasiclassical approximation for the rotational degrees of freedom, the collision probability can depend only on invariant combinations of nonspherical variables that are constants of the rotational motion and, at the same time, are invariant under symmetry transformations of the point symmetry group of the molecule. This property of the collision probability averaged over rapid rotations ensures that a symmetric molecule does not exhibit cross effects such as viscosity—thermal conductivity in an external field,[8,15-18] i.e., it does not lead to the diagonalization of the matrix of transport coefficients. Point symmetry of nonspherical molecules, in general, leads to a simplification of the selection rules for the matrix elements of the collision operator. These selection rules, in turn, enable us to establish the nature of the polarization of angular momenta that appears in the nonequilibrium state.

In Sec. 2, we shall investigate the properties of the nonspherical-collision operator that are responsible for the appearance of polarization of angular momenta in nonequilibrium states and, in Sec. 3, these properties will be used to explain the anomalous behavior of the components of the thermal conductivity tensor for the CH_3CN gas in an electric field.

2. PROPERTIES OF THE NONSPHERICAL-COLLISION OPERATOR

It is well known that the field dependence of the transport coefficients is due to the nonspherical nature of scattering by rotating molecules. We shall therefore write the collision operator in the form of the sum

$$\Omega=\Omega_0+\Omega_1, \tag{2.1}$$

where Ω_0 represents the spherically symmetric part of the collision probability and Ω_1 describes collisions involving a change in the direction of the angular momentum. To investigate the properties of Ω_1, we introduce a set of basis vectors $|\nu\rangle$ that are orthogonal with weight f_0, where f_0 is the local equilibrium distribution. For molecules in the form of a symmetric spinning top, we have

$$|\nu\rangle=|r_1H_1h_1,\ r_2H_2h_2\tau\rangle, \tag{2.2}$$

where the set of indices $(r_1H_1h_1)$ determines the dependence of the basis vector on the velocity **u**, the set of indices $(r_2H_2h_2\tau)$ describes the dependence on the angular momentum **M**, the indices H_1h_1 characterize the dependence on the direction of the velocity vector, and $H_2h_2\tau$ specify the dependence on the direction of the angular momentum in the laboratory frame and in the frame attached to the molecule. We note that the basis vectors $|\nu\rangle$ must be invariant under transformations belonging to the point symmetry group of the molecule, and can depend only on combinations of nonspherical variables that are the constants of rotational motion.[14] Thus, for example, averaging over rapid rotations in the case of asymmetric molecules leads to the effective point symmetry group D_{2h} (the "symmetry" of the function f_0). Since the symmetry elements of this group include both inversion and reflection in a plane, the collision probability averaged over rapid rotations is invariant under space inversion. Consequently, in the zero-order approximation in $\omega_0\tau_c$ (ω_0 is the frequency of free rotation of the molecule and τ_c^{-1} is the collision frequency), cross effects such as viscosity-thermal conductivity, which are possible for stereoisomeric gases in a magnetic field,[17,18] are absent. For molecules in the form of a symmetric spinning top, invariance under the transformations of the point symmetry group of the molecule ensures that odd values of τ (the values of τ determine the dependence of the vector $|\nu\rangle$ on the orientation of the angular momentum in the coordinate frame attached to the molecule) are possible only for molecules with point symmetry C_{nv}.

Since the operator Ω_1 is a scalar, its matrix elements are given by

$$\langle\nu'|\Omega_1|\nu\rangle=\sum_{Nn}\langle H_1'h_1'H_2'h_2'|Nn\rangle\langle H_1h_1H_2h_2|Nn\rangle\langle\mu'|\Omega_1|\mu\rangle, \quad (2.3)$$

where $|\mu\rangle=r_1r_2H_1H_2Nn,\tau\rangle$ and $\langle H_1h_1H_2h_2|Nn\rangle$ is the Clebsch-Gordon coefficient. To investigate the matrix $\langle\mu'|\Omega_1|\mu\rangle$, the operator Ω_1 can be written in the form

$$\begin{gathered}\Omega_1=\Omega^{(1)}+\Omega^{(2)}-\Omega^{(3)}-\Omega^{(4)},\\ \langle p|\Omega^{(1)}|s\rangle=\mathrm{Sp}\,f_0f_{01}\varphi_p{}^*\varphi_s w,\quad \langle p|\Omega^{(2)}|s\rangle=\mathrm{Sp}\,f_0f_{01}\varphi_p{}^*\varphi_{1s}w,\\ \langle p|\Omega^{(3)}|s\rangle=\mathrm{Sp}\,f_0f_{01}\varphi_p{}^*\varphi_s'w',\quad \langle p|\Omega^{(4)}|s\rangle=\mathrm{Sp}\,f_0f_{01}\varphi_p{}^*\varphi_{1s}'w',\end{gathered} \quad (2.4)$$

where subscript 1 refers to a molecule participating in the collision and the prime indicates functions that depend on the post-collision variables. Each of the operators $\Omega^{(i)}$ in (2.4) will be written in the form of the sum

$$\begin{gathered}\Omega^{(i)}=\Omega_+^{(i)}+\Omega_-^{(i)},\\ \Omega_+^{(i)}={}^1/_2(\Omega^{(i)}+\Omega^{(i)+}),\quad \Omega_-^{(i)}={}^1/_2(\Omega^{(i)}-\Omega^{(i)+}),\end{gathered} \quad (2.5)$$

where the superscript + represents Hermitian conjugation. Using (2.4) and the relation $\mathrm{Sp}_{1'2'}w=\mathrm{Sp}_{1'2'}w'$,[14] we obtain

$$\begin{aligned}&\Omega_-^{(1)}=0,\\ &\Omega_+^{(1,2)}=0 \quad \text{for} \quad w(1,2\to1',2')=-w(1',2'\to1,2),\\ &\Omega_-^{(2)}=0 \quad \text{for} \quad w(1,2\to1',2')=w(2,1\to2',1'),\\ &\Omega_\pm^{(3)}=0 \quad \text{for} \quad w(1,2\to1',2')=\mp w(1',2'\to1,2),\\ &\Omega_\pm^{(4)}=0 \quad \text{for} \quad w(1,2\to1',2')=\mp w(2',1'\to2,1).\end{aligned} \quad (2.6)$$

It is clear from (2.6) that, if the probabilities of direct and inverse collisions are not equal, the collision operator will not be Hermitian. In fact, the anti-Hermitian part of this operator is connected only with the operators $\Omega^{(3)}$ and $\Omega^{(4)}$ which, clearly, describe the departure of the moles from the Γ state (Γ is the set of variables necessary to describe the molecule) due to collisions per unit volume.

It is well known that, for particles with internal degrees of freedom, the relationship between the probabilities of direct and inverse collisions is

$$w(1,2\to1',2')=w(1_T',2_T'\to1_T,2_T), \quad (2.7)$$

where the state 1_T is that in which the velocity and angular momentum change their signs. This relation reflects the symmetry of the collision probability under time reversal. In the case of rotational degrees of freedom, the internal state of the molecule in the form of a symmetric spinning top is determined by the quantum numbers J,M,K, where M and K are the components of the angular momentum along the external and internal axes. There is degeneracy in M and in the sign of K. Because of this degeneracy, we can select any combination of degenerate functions. Let us therefore consider states $|JKMP\pi\rangle$ of the form

$$\begin{aligned}|JKMP\pi\rangle=\frac{1}{2}\{&|JKM\rangle+(-1)^P\eta_I|J-KM\rangle\\ &+(-1)^\pi\eta_T|J-K-M\rangle+(-1)^{P+\pi}\eta_I\eta_T|JK-M\rangle\},\end{aligned} \quad (2.8)$$

where $P=0$, 1; $P=0$, $\pi=0$, 1 for $K=0$, and $\pi=0$ for $M=0$. The phase factors η_I and η_T in (2.8) are determined in accordance with

$$\hat{I}|JKM\rangle=\eta_I|J-KM\rangle,\quad \hat{T}|JKM\rangle=\eta_T|J-K-M\rangle, \quad (2.9)$$

where $\hat{I}$ and $\hat{T}$ are the space inversion and time reversal operators. Using (2.8) and (2.9) we find that

$$\begin{aligned}&\langle\mathbf{k}',J'K'M'P'\pi'|\mathcal{T}|\mathbf{k},JKMP\pi\rangle\\ &=(-1)^{\Delta\pi}\langle-\mathbf{k},JKMP\pi|\mathcal{T}|-\mathbf{k}',J'K'M'P'\pi'\rangle\\ &=(-1)^{\Delta P+\Delta\pi}\langle\mathbf{k},JKMP\pi|\mathcal{T}|\mathbf{k}',J'K'M'P'\pi'\rangle,\end{aligned} \quad (2.10)$$

where $\mathcal{T}$ is the scattering matrix, $\mathbf{k}$ is the wave vector of the molecule, and $\Delta f=f'-f$ is the change in f in a collision. If we use (2.10), we obtain the much simpler result

$$w(1\ 2\to1',2')=w(1',2'\to1,2). \quad (2.11)$$

for the collision probability which is proportional to the square of the modulus of the matrix element of the scattering matrix. When an external field is present, the choice of linear combinations of degenerate functions ceases to be arbitrary if the wave functions are subjected to the requirement that the applied field produces a small change in them (small perturbation). This condition will be satisfied when the nondiagonal matrix elements of the perturbation operator are small in comparison with the diagonal matrix elements. The functions introduced in (2.8) do not satisfy this condition because, for these functions, the matrix elements with different P and π are not small. Moreover, the change in the functions $|JKM\rangle$ or the quasiclassical functions $|J\theta\varphi\sigma\psi\rangle$[14] is small, i.e., we can use the usual perturbation theory methods. For transitions between the states $|JKM\rangle$ or $|J\theta\varphi\sigma\psi\rangle$, only (2.7) is satisfied. However, for molecules with a definite point symmetry, the relation given by (2.11) can be obtained from (2.7) for the chosen model based on nonspherical potential scattering.[11-13]

Thus, for molecules that do not have optical isomers, the probability of collision is unaffected by space inversion or time reversal. These symmetry properties lead to selection rules for the collision operator.[20] In our notation, these rules have the following form:

$$\begin{aligned}H_1'+H_1+\tau'+\tau &\quad \text{even} \quad \text{for} \quad \Omega_+ \text{ and } \Omega_-,\\ H_2'+H_2 &\quad \text{even} \quad \text{for} \quad \Omega_+,\\ H_2'+H_2 &\quad \text{odd} \quad \text{for} \quad \Omega_-.\end{aligned} \quad (2.12)$$

For molecules with a definite point symmetry, the selection rules given by (2.12) can be simplified by evaluating the integrals with respect to the angular variables in the matrix elements of the operator Ω_1. From the point of view of the momentum conversion law, it is convenient to introduce the variables c_Δ and c_Σ which are related to the relative velocity and the center of mass, as follows[1)]

$$c_\Delta=\frac{1}{\sqrt{2}}(c-c_1),\quad c_\Sigma=\frac{1}{\sqrt{2}}(c+c_1). \tag{2.13}$$

After integration with respect to the velocity of the center of mass (see Appendix A), we obtain

$$\langle\mu'|\Omega_1|\mu\rangle=\sum_{\substack{A_1'A'A_1A\\B_1BQ}}\langle\eta'|\Omega_1|\eta\rangle\Pi_{QQH_1'H_1}(-1)^{\Delta H_1+\Delta H_2}\times\begin{Bmatrix}H_1'A'B\\QNH_2'\end{Bmatrix}\begin{Bmatrix}BAH_1\\H_2NQ\end{Bmatrix}F^{r_1'H_1'}_{A_1'A'B_1B}F^{r_1H_1}_{A_1AB_1B}, \tag{2.14}$$

where $|\eta\rangle=|A_1r_2,AH_2Qq,\tau\rangle$. The matrices of the operator Ω_1 on the left-and right-hand sides of (2.14) have the same form if we make the following formal substitutions in the matrix elements $\langle\mu'|\Omega_1|\mu\rangle$:

$$\begin{gathered}\exp(-c^2-c_1^2)\to\exp(-c_\Delta^2),\\ c\to c_\Delta,\quad c_1\to-c_\Delta,\quad c'\to c_\Delta',\quad c_1'\to-c_\Delta'.\end{gathered} \tag{2.15}$$

and modify the indices in the appropriate fashion. The only terms that are nonzero in (2.14) are those for which

$$\begin{gathered}r_1'+H_1'/2=A_1'+A'/2+B_1+B/2,\quad r_1+H_1/2=A_1+A/2+B_1+B/2,\\ A'+A+\tau'+\tau-\text{even}.\end{gathered} \tag{2.16}$$

The following relations then follow from (2.16) for integer values of the indices:

$$\begin{gathered}A'+A\ \text{even}\quad\text{for}\quad H_1'+H_1\ \text{even}\\ A'+A\ \text{odd}\quad\text{for}\quad H_1'+H_1\ \text{odd}\end{gathered} \tag{2.17}$$

To evaluate the integrals with respect to the angular variables in the matrix elements $\langle\eta'|\Omega_1|\eta\rangle$, we write the collision probability in the form of an expansion in terms of spherical tensors that depend on the directions of the velocities and the angular momenta of the colliding molecules

$$w=\sum_{\Lambda}W_\Lambda(Z)[l'\otimes l]_L\cdot\{[s'\otimes s]_T\otimes[s_1'\otimes s_1]_{T_1}\}_L, \tag{2.18}$$

where $Z=(c_\Delta'c_\Delta,J'JJ_1',x'xx_1'x_1)$ and Λ represents the set of indices $(l'lL,s'sT,s_1's_1T_1)$. To abbreviate the notation in (2.18), the spherical tensor of rank s is represented simply by the symbol s. The dependence on the directions of the velocities is represented by the symbols l' and l, and the dependence on the directions of the angular momenta is represented by the symbols $s'ss_1's_1$. Each spherical tensor of rank L in (2.18) is defined with the phase factor i^L. The coefficients $W_\Lambda(Z)$ are then real functions.

To ensure that the collision probability is invariant under space inversion, the coefficients W_Λ in (2.18) must satisfy the relation

$$W_\Lambda(Z)=(-1)^{l+l'}W_\Lambda(Z_I), \tag{2.19}$$

where $Z_I=(c_\Delta'c_\Delta,J'JJ_1'J_1,-x'-x-x_1'-x_1)$. In precisely the same way, invariance of the collision probability under time reversal yields

$$W_\Lambda(Z)=(-1)^{T+T_1+L}W_{\Lambda_T}(Z_T), \tag{2.20}$$

where

$$\Lambda_T=(ll'L,ss'T,s_1s_1'T_1),\quad Z_T=(c_\Delta c_\Delta',JJ'J_1J_1',-x-x'-x_1-x_1').$$

It is clear from (2.19) and (2.20) that the probabilities of direct and inverse collisions will not be equal only when the coefficients W_Λ in (2.18), for which $s'+s+s'_1+s_1$ is an odd number, are not zero. In other words, the departure from the equation $w=w'$ in the case of molecules that do not have optical isomers is due to expansion terms that are odd in the angular momenta of the colliding molecules. We also note that it follows from $\mathrm{Sp}_{1,2}w=\mathrm{Sp}_{1',2'}w'$ that, for $s'=s_1'=l'=0$, only those W_Λ are nonzero for which $s+s_1$ is even (condition I).

After integrating with respect to the angles, we obtain

$$\begin{gathered}\langle\eta'|\Omega^{(i)}|\eta\rangle=\sum_L\langle\lambda'|\Omega_{\Lambda_i}|\lambda\rangle4\pi\Pi_L^2(-1)^{Q+L}\begin{Bmatrix}AH_2Q\\H_2'A'L\end{Bmatrix}[\eta'\eta]_i^{(L)},\\ [\eta'\eta]_1^{(L)}=i^{A+A'+H_2+H_2'}\Pi_{A'H_2'}\langle A'0L0|A0\rangle\langle H_2'0L0|H_20\rangle,\\ [\eta'\eta]_2^{(L)}=i^{A+A'+L}(-1)^{A+H_2'}\Pi_{A'}\langle A'0L0|A0\rangle,\quad[\eta'\eta]_3^{(L)}=(-1)^{A+H_2'}\\ [\eta'\eta]_4^{(L)}=(-1)^{H_2'}.\end{gathered} \tag{2.21}$$

In these expressions,

$$\begin{gathered}|\lambda\rangle=|A_1Ar_2H_2r\rangle,\quad\Lambda_1=(0LL,0LL,000),\quad\Lambda_2=(0LL,0H_2'H_2',0H_2H_2),\\ \Lambda_3=(A'AL,H_2'H_2L,000),\quad\Lambda_4=(A'AL,H_2'0H_2',0H_2H_2),\end{gathered}$$

and the subscript Λ_i in the matrix element $\langle\lambda'|\Omega_{\Lambda_i}|\lambda\rangle$ indicates that it is defined with the coefficient W_{Λ_i} in the expansion given by (2.18). When the transport coefficients (thermal conductivity, viscosity) of molecular gases are determined, one is interested only in "transitions from the state" with $H_2=0$ because the macroscopic homogeneity does not then depend on the direction of the angular momentum. The presence of the $6j$ symbol in (2.21) then leads to the condition $H_2'=L$ (condition II). Conditions I and II and also (2.16) can readily be used to obtain the following selection rules for the operators $\Omega_{\lambda1}$ and $\Omega_{\lambda2}$:

$$\left.\begin{matrix}A'+A\\H_2'+H_2\\\tau'+\tau\end{matrix}\right\}\quad\text{even}; \tag{2.22}$$

where and henceforth $H_2=0$.

It follows from (2.21) that condition I is not valid for $i=3,4$. Using condition II, we note that the restrictions on the allowed values of $H_2'+H_2$ are only possible if the values of L are determined by the point symmetry of the colliding molecules. On the other hand, it follows from (2.19) that the allowed values of $l+l'$ always depend on the point symmetry of the molecule. Consequently, when the allowed values of $H_2'+H_2$ are restricted, the values of $l+l'+L$ must be even (condition III). It can be shown on the basis of published results[14,19] that condition III will be satisfied for the distorted-wave approximation, widely used in scattering theory, if the distorting potential is taken to be the spherical part of the interaction between the molecules. From (2.16), (2.21), and condition III, we obtain the selection rules for the operators $\Omega_{\Lambda3}$ and $\Omega_{\Lambda4}$:

$$\left.\begin{array}{l}A'+A\\H_2'+H_2\\\tau'+\tau\end{array}\right\}\ \text{even},\quad\left.\begin{array}{l}A'+A\\H_2'+H_2\\\tau'+\tau\end{array}\right\}\ \text{odd}\tag{2.23}$$

Thus, in accordance with (2.17), (2.22), and (2.23), the selection rules for the operators Ω_+ and Ω_- are as follows:

$$\left.\begin{array}{l}H_1'+H_1\\H_2'+H_2\\\tau'+\tau\end{array}\right\}\ \text{even}\quad\left.\begin{array}{l}H_1'+H_1\\H_2'+H_2\\\tau'+\tau\end{array}\right\}\ \text{odd},\tag{2.24}$$

where, in the above approximation, the matrix elements of the operator Ω_- are nonzero only for molecules with symmetry C_{nv}. We note in this connection that the anomalous Senftleben effect is observed in gases consisting of the molecules with C_{3v} symmetry,[9] and that, by using the selection rules given by (2.24), we can verify the absence of viscosity-thermal conductivity cross effects that has been predicted[8,15,16] for molecules in the form of a symmetric spinning top.

3. THERMAL CONDUCTIVITY OF CH_3CN GAS IN AN ELECTRIC FIELD

The formal solution of the transport equation for molecules with rotational degrees of freedom in an electric field will be written in the form[2)]

$$\begin{gathered}\chi_{ln}=(\Omega+\Omega_E)^{-1}A_{ln}=\{1-(\Omega_0+\Omega_E)^{-1}\Omega_1+(\Omega_0+\Omega_E)^{-1}\Omega_1(\Omega+\Omega_E)^{-1}\Omega_1\}\chi_{ln}^{(0)}\\\chi_{ln}^{(0)}=(\Omega_0+\Omega_E)^{-1}A_{ln}=\Omega_0^{-1}A_{ln},\end{gathered}\tag{3.1}$$

where Ω_E describes the precession of the molecules in the electric field[14] and the functions A_{ln} characterize the given macroscopic inhomogeneity.[20] Using (3.1), we obtain

$$\Delta[\langle A_{ln}|\chi_{ln}\rangle]=\langle\chi_{ln}^{(0)}|\Omega_1K\Omega_1|\chi_{ln}^{(0)}\rangle,\quad K=(\Omega+\Omega_E)^{-1}-\Omega^{-1},\tag{3.2}$$

where $\Delta\Phi$ is the change in Φ in the field. We note that we have not assumed in the derivation of (3.2) that the change in the collision probability with changing orientation of the angular momentum is small. Using (3.2), we obtain the following expressions for the heat flux components $q^{\parallel}(\mathbf{E}\parallel\nabla T)$ and $q^{\perp}(\mathbf{E}\perp\nabla T)$:

$$\begin{gathered}q^{\parallel}=\varkappa^{\parallel}\nabla T,\quad q^{\perp}=\varkappa^{\perp}\nabla T,\\\Delta\varkappa^{\parallel}=\varkappa^{\parallel}-\varkappa_0=\frac{4\pi}{3}\langle\chi_{10}^{(0)}|\Omega_1K\Omega_1|\chi_{10}^{(0)}\rangle,\\\Delta\varkappa^{\perp}=\varkappa^{\perp}-\varkappa_0=\frac{4\pi}{3}\operatorname{Re}\langle\chi_{11}^{(0)}|\Omega_1K\Omega_1|\chi_{11}^{(0)}\rangle,\end{gathered}\tag{3.3}$$

where $\varkappa_0$ is the thermal conductivity in the absence of the external field. Henceforth, the formulas for the perpendicular effect ($\Delta\varkappa^{\perp}$) will be written out only when they are substantially different from the analogous formulas for the parallel effect ($\Delta\varkappa^{\parallel}$). The expressions for $\Delta\varkappa^{\parallel}$ can be written in following way with the aid of the operators Ω_+ amd Ω_-, introduced in Sec. 2:

$$\begin{gathered}\Delta\varkappa=\Delta\varkappa_+^{\parallel}+\Delta\varkappa_-^{\parallel},\\\Delta\varkappa_+^{\parallel}=-\frac{4\pi}{3}\sum_{\nu}|\langle\nu|\Omega_-|0\rangle|^2K_{\nu\nu},\\\Delta\varkappa_-^{\parallel}=\frac{4\pi}{3}\sum_{\nu}|\langle\nu|\Omega_+|0\rangle|^2K_{\nu\nu},\end{gathered}\tag{3.4}$$

where $|0\rangle=\chi_{10}^{(0)}$. In deriving (3.4), we have neglected the nondiagonal matrix elements of the operator K, which corresponds to the frequently valid assumption that the nondiagonal matrix elements of the operator Ω are small.

Comparison with experiment has shown[10] that, for molecular gases with the normal Senftleben effect, we can confine our attention in (3.4) to terms of the form $|\nu_H\rangle=|01h_1,02h_2,0\rangle$, which describe collisions with a reorientation of the angular momentum. We note that, in the Cartesian set of coordinates, the term $|\nu_H\rangle$ corresponds to the vector $\mathbf{u}\cdot[\mathbf{M}]^{(2)}$ ($[\mathbf{a}]^{(2)}$ is an irreducible tensor of rank 2) which is referred to as the Kagan vector in the literature. This simplified two-moment approximation is inconvenient in the case of the anomalous Senftleben effect because, in addition to the term $\mathbf{u}\cdot[\mathbf{M}]^{(2)}$, one must then also take into account the terms that are odd in the angular momentum and appear as a result of collisions described by the anti-Hermitian part of the operator Ω. From the phenomenologic point of view, the simplest term of this type is the Waldmann vector $[\mathbf{u}\,\mathbf{M}]$. This vector is widely used at present in the study of effects due to nonspherical interactions between molecules (detailed information can be found in the literature[1,10]). However, in contrast to Kagan's vector, the applicability of the Waldmann vector is not as well justified because of the large number of parameters that is necessary to describe the experimental data. Moreover, it follows from (2.24) that the Waldmann vector is forbidden by selection rules in the case of the model based on nonspherical potential scattering.[11-13] In addition, when the positive change in the thermal conductivity in a field is described with the aid of the Waldmann vector, it is not possible to explain the absence of the anomalous behavior in a mixture of monatomic and polar gases for low concentrations of the latter.[21] This feature of the anomalous Senftleben effect can easily be explained if it is assumed that the operator Ω_- describes collisions with a change in the component of the angular momentum along the axis of the spinning top. As a matter of fact, for symmetric top molecules, such collisions correspond to spherical tensors in the expansion of the scattering matrix $\mathcal{T}$ for which $l\geqslant3$ for scattering by the molecule and $l\geqslant6$ for scattering by the atom.[19] It is clear that, if nonspherical expansions of the matrix $\mathcal{T}$ converge rapidly, terms with $l\geqslant6$ can be neglected.

Collisions with a change in the component of the angular momentum along the spinning-top axis ensure that the nonequilibrium distribution function of the gas molecules depends on $x=\cos\sigma$. In view of this, and because of the selection rules given by (2.24), we choose the vector $[\mathbf{u}]^{(2)}\cdot\mathbf{M}x$ for the description of the positive change in the thermal conductivity when $\mathbf{E}\parallel\nabla T$, which corresponds to $|\nu_a\rangle=|02h_1,01h_2,1\rangle$. This model leads to the following expression for the relative change in $\varkappa^{\parallel}$ in the field:

$$\begin{gathered}\delta\varkappa_-^{\parallel}=-0.6\psi_h\mathcal{J}_1(\gamma_h,\varkappa),\quad\delta\varkappa_+^{\parallel}=0.6\psi_a\mathcal{J}_2(\gamma_a,\varkappa),\\\mathcal{J}_1(\gamma_h,\varkappa)=\frac{2}{\pi^{1/2}}\frac{\varkappa^{5/2}}{\varkappa^2+{}^1/_2\varkappa+{}^3/_8}\int\limits_0^1dx\int\limits_0^\infty dJ\,J^6\exp\{-J^2[1+(\varkappa-1)x^2]\}\frac{(\gamma_hx/J)^2}{1+(\gamma_hx/J)^2}\\\mathcal{J}_2(\gamma_a,\varkappa)=\frac{8}{\sqrt{\pi}}\varkappa^{3/2}\int\limits_0^1dx\,x^2\int\limits_0^\infty dJ\,J^4\exp\{-J^2[1+(\varkappa-1)x^2]\}\frac{(\gamma_ax/J)^2}{1+(\gamma_ax/J)^2},\end{gathered}\tag{3.5}$$

$$\psi_s=\frac{4\pi}{3}\frac{\Omega_{s0}^2}{\omega_s\varkappa_0},\quad \gamma_s=\frac{E}{p}g_s,\quad g_s=d\left(\frac{A}{T}\right)^{1/2}\left(\frac{\omega_s}{p}\right)^{-1},\quad s=k,a,$$

where d is the dipole moment of the molecule, p is the gas pressure, Ω_{s0} and ω_s are the matrix elements of the operator Ω:

$$\Omega_{s0}=\langle\mu_s|\Omega|0\rangle,\quad \omega_s=\langle\nu_s|\Omega|\nu_s\rangle, \tag{3.6}$$

and the general definition of the vectors $|\mu\rangle$ and $|\nu\rangle$ is given in Sec. 2. We note, in particular, that $|\mu_k\rangle=|00, 1210, 0\rangle$, $|\mu_a\rangle=|00,2110, 1\rangle$.

The expression for the relative change in $\varkappa^{\perp}$ in a field can be obtained in similar way. However, in addition to the vector $[\mathrm{u}]^{(2)}\cdot\mathrm{M}x$, we now take into account $\mathrm{M}x$, which is allowed by the selection rules but does not contribute to the parallel effect. The result is

$$\begin{aligned}\delta\varkappa_{-}{}^{\perp}&=-0.6\psi_k[0.5\mathcal{I}_1(\gamma_k,\varkappa)+\mathcal{I}_1(2\gamma_k,\varkappa)],\\ \delta\varkappa_{+}{}^{\perp}&=0.7\psi_a\mathcal{I}_2(\gamma_a,\varkappa)+\psi_b\mathcal{I}_2(\gamma_b,\varkappa),\end{aligned} \tag{3.7}$$

where the subscript b refers to the vector $\mathrm{M}x$, $|\mu_b\rangle=|00,0111,1\rangle$, and the remaining notation is similar to that in (3.5). The integrals $\mathcal{I}_1(\gamma,\varkappa)$ in (3.5) and (3.7) cannot be expressed in terms of elementary functions and must be evaluated approximately. Using the formulas given in Appendix C, we obtain the following results for the CH_3CN molecule ($\varkappa=17.3$):

$$\begin{aligned}\mathcal{I}_1(\gamma_k;17.3)&\approx\left[\frac{\pi_kE/p}{1+\pi_kE/p}\right]^2,\quad \pi_k=0.118g_k,\\ \mathcal{I}_2(\gamma_a;17.3)&\approx\left[\frac{\pi_aE/p}{1+\pi_aE/p}\right]^2,\quad \pi_a=0.913g_a.\end{aligned} \tag{3.8}$$

To determine the theoretical parameters ψ_s and π_s ($s=k$, a, b) in (3.5) and (3.7), it is convenient to use a graphical method similar to that described by De Groot *et al.*[22] It then turns out that a single set of parameters ψ_s, g_s cannot describe the experimental functions $\delta\varkappa^{\parallel}=\varphi(E/p)$ and $\delta\varkappa^*=3/5\,\delta\varkappa^{\parallel}+2/5\,\delta\varkappa^{\perp}=\psi(E/p)$ to within experimental error (about 10%). To describe the experimental results in this case, one must take into account the nondiagonal matrix elements of $\Omega_{s's}$ in the evaluation of the matrix of the operator K in (3.4). It is shown in Appendix C that, in this case, one must substitue $\psi_s\to\psi_s^{\parallel}$ (for the parallel effect) and $\psi_s\to\psi_s^{\perp}$ (for the perpendicular effect) in (3.5) and (3.7). This procedure was used to obtain the set of parameters $\psi_s^{\perp}$, $\psi_s^{\parallel}$, π_s that is in satisfactory agreement with experimental data. The figure shows the experimental and theoretical results for $\delta\varkappa^{\parallel}$ and $\delta\varkappa^*$. The theoretical parameters are listed below (the asterisks indicate the field dependence of $\delta\varkappa^*$):

Parameter:	ψ_k^*	$\psi_k^{\parallel}$	ψ_a^*	$\psi_a^{\parallel}$	ψ_b^*	π_k	π_a	π_b
Result in units of 10^{-3}	7.83	7.62	7.27	7.54	1.86	1.60	1.80	5.30

The dimensions of π_s are $(\mathrm{V\cdot cm/Torr})^{-1}$. The precision to which ψ_s, π_s are calculated corresponds to the experimental error (about 10%).

The calculated valus of π_s enable us to calculate the effective collision frequency ω_s/p. The result is:

$$\omega_k/p=35.2\cdot10^6,\quad \omega_b/p=82.2\cdot10^6,$$
$$\omega_a/p=242.1\cdot10^6,\quad \omega/p=18.8\cdot10^6.$$

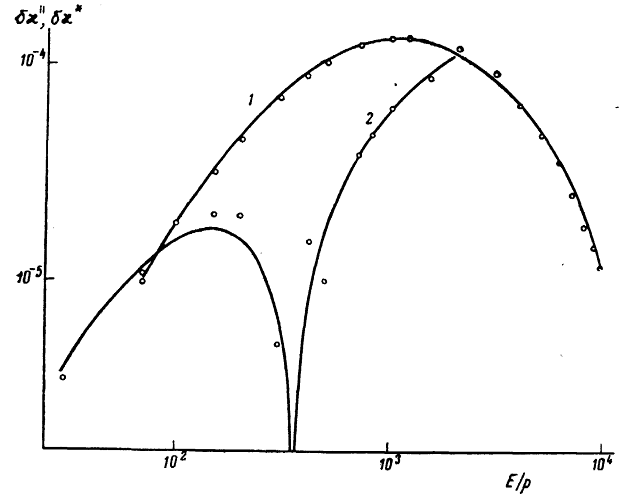

FIG. 1. Relative change in the thermal conductivity as a function of E/p (double logarithmic scale): 1—$\delta\varkappa^{\parallel}=\varphi(E/p)$; 2—$\delta\varkappa^*=\psi(E/p)$ for CH_3CN gas.

The ratio ω_s/p is given in $\mathrm{sec^{-1}\cdot Torr^{-1}}$.

For comparsion, we also give the effective frequency of elastic collisions $\omega/p=\eta^{-1}$,[23] where η is the viscosity. We note that the figure $\omega_b/p=82.2$ characterizing the effective collision frequency for the polarization $\mathrm{M}x$ is in agreement with the result $\omega_b/p=75.4$, deduced from measurements of nonresonance absorption in CH_3CN gas.[24]

It is clear from the formulas in Appendix C that $\psi_s^{\parallel}$ and $\psi_s^{\perp}$ are proportional to the matrix element of the operator Ω^{-1}. In general, the operator Ω^{-1} is nondiagonal not only in the indices $H_1H_2\tau$, but also in the projections h_1 and h_2. This leads to an increase (as compared with the diagonal approximation) in the number of parameters in the theory. To determine these parameters, one must, naturally, increase the number of independent experiments. We note that this can be done by investigating the anomalous behavior of the thermal conductivity of CH_3CN gas in a magnetic field. Unfortunately, however, this information is lacking at present. On the other hand, the data reported by Borman *et al.*,[25] who investigated the perpendicular anomalous magnetic Senftleben effect in the case of CH_3CN gas, give rise to some doubt because they can only be explained by assuming that the CH_3CN molecule has an anomalously large magnetic moment.[23]

It is clear from the foregoing discussion that the field dependence of both $\delta\varkappa^{\parallel}$ and $\delta\varkappa^{\perp}$ must be known if one wishes to obtain complete information on the polarization characteristics of the anomalous Senftleben effect. Such experiments have so far been performed only for CH_3CN gas. However, some qualitative predictions about the anomalous behavior of other polar gases can be made on the basis of the concept of effective symmetry. As an example, consider the effect for the CH_3F and CHF_3 molecules. These molecules ($d_{CH_3F}=1.86D$; $d_{CHF_3}=1.64D$) are symmetric spinning tops and have the symmetry C_{3v}. Moreover, studies of the parallel effect in these gases have shown[22] that CHF_3 differs from CH_3F in that it does not exhibit an increase in the thermal conductivity even for small values of the ratio E/p. This behavior may be due to the fact that the terms in the nonspherical expansion (2.18) with odd values of L, which provide the contribution to the anti-Hermittian part of the collision operator, are more important for CHF_3 than for CH_3F. The "light" H atom in CHF_3 is located at a shorter distance from the c atom than the "heavy" F atom in the CH_3F molecule. For nonspherical collisions, therefore, the effective symmetry of the CHF_3 molecule may be the same as the symmetry of the planar molecue, i.e., D_{3h}. On the other hand, for molecules of this symmetry, odd values of L are forbidden by symmetry considerations.[13,25] We note that the Kagan vector is sufficient in this case for the description of the field effect and, as is well known, $[\delta\varkappa^{\perp}/\delta\varkappa^{\parallel}] = 3/2$ in this case for $E \to \infty$. A similar analysis is valid for the NF_3 molecule ($d_{NF_3} = 0.234D$), in which the nitrogen atom is located close to the plane passing through the fluorine atom, so that the effective symmetry of the molecule is D_{3h}. For the NF_3 gas, the measured value of $[\delta\varkappa^{\perp}/\delta\varkappa^{\parallel}]$ for $E \to \infty$ is 1.56.[26] In contrast to CH_3F, the symmetry of the CH_3CN molecule ($d_{CH_3CN} = 3.92D$) is an elongated symmetric top, and this is clearly different from the symmetry of the planar molecule.

In conclusion, the author regards it as his pleasant duty to thank U.M. Kagan, L.A. Maksimov, A.A. Ovchinnikov, V.D. Borman, B.I. Nikolaev, and V.I. Troyan for discussions and valuable advice.

APPENDIX A

The dependence of the basis vector $|\nu\rangle$ in (2.2) on the velocity $\mathbf{u}$ is described by the function

$$\Phi_{r_1H_1h_1}(\mathbf{u}) = \left[\frac{2\pi^{3/2} r_1!}{\Gamma(r_1+H_1+3/2)}\right]^{1/2} L_{r_1}^{H_1+1/2}(u^2)\, u^{H_1} i^{H_1} Y_{H_1h_1}(\hat{\mathbf{u}}), \qquad \text{(A.1)}$$

where $\Gamma(x)$ is the gamma function, $L_r^l(x)$ is the Laguerre polynomial, and $Y_{lm}(\hat{\mathbf{x}})$ are spherical harmonics. To evaluate the integral with respect to the velocity of the center of mass, we need a formula relating the function $\Phi_{rHh}[2^{-1/2}(\mathbf{c}_\Delta + \mathbf{c}_\Sigma)]$ to the functions $\Phi_{A_1A\alpha}(\mathbf{c}_\Delta)$ and $\Phi_{B_1B\beta}(\mathbf{c}_\Sigma)$. Let q be the sum of the vectors a and b, and consider the function $b_l(q)Y_{lm}(\mathrm{q})$. Using the δ-function representation, we obtain

$$b_l(q)\,Y_{lm}(\hat{\mathbf{q}}) = (2\pi)^{-3}\int d\mathbf{x}\, b_l(x)\, Y_{lm}(\hat{\mathbf{x}}) \int d\mathbf{r} \exp[i\mathbf{r}(\mathbf{x}-\mathbf{q})]. \qquad \text{(A.2)}$$

Having evaluated the integrals with respect to the angles in (A.2), and using the well-known expansion for a plane wave, we obtain

$$\Pi_l b_l(q)\, i^l Y_{lm}(\hat{\mathbf{q}}) = \sum_{A,B} 4\pi^{-1/2}\Pi_{AB}\langle A0B0|l0\rangle B_{lAB}(a,b)\, i^{A+B}[Y_A(\hat{\mathbf{a}})\otimes Y_B(\hat{\mathbf{b}})]_{lm},$$

$$B_{lAB}(a,b) = \int_0^\infty dx\, x^2 b_l(x) \int_0^\infty dr\, r^2 j_l(xr)\, j_A(ar)\, j_B(br), \qquad \text{(A.3)}$$

$$\Pi_{xy\ldots} = [(2x+1)(2y+1)\ldots]^{1/2},$$

where $j_l(x)$ is the spherical Bessel function and the symbol ⊗ represents the irreducible tensorial product of spherical tensors. Using (A.3) and the expansion of the spherical Bessel function in terms of the Lagurre polynomials, we obtain

$$\Phi_{rHh}\left[\frac{1}{\sqrt{2}}(\mathbf{c}_\Sigma + \mathbf{c}_\Delta)\right] = \sum_{A_1AB_1B} F^{rH}_{A_1AB_1B}[\Phi_{A_1A}(\mathbf{c}_\Delta)\otimes\Phi_{B_1B}(\mathbf{c}_\Sigma)]_{Hh},$$

$$F^{rH}_{A_1AB_1B} = \left[\frac{\Gamma(3/2)\Gamma(r+H+3/2)\,r!}{\Gamma(A_1+A+3/2)\Gamma(B_1+B+3/2)A_1!B_1!}\right]^{1/2}\frac{\Pi_{AB}}{\Pi_H}2^{-r-H/2}\langle A0B0|H0\rangle, \qquad \text{(A.4)}$$

where the nonzero terms in the sum are those for which $r + H/2 = A_1 + A/2 + B_1 + B/2$.

APPENDIX B

We shall now derive the approximate formula for the integrals $\mathcal{T}_1(\gamma,\varkappa)$ and $\mathcal{T}_2(\gamma,\varkappa)$. Using the Bürmann expansion,[27]

$$\frac{\gamma^2p^2}{1+\gamma^2p^2} = \sum_{n=1}^{\infty}\frac{1}{n!}\left(\frac{\xi\gamma}{1+\xi\gamma}\right)^n\left\{\frac{d^{n-1}}{d\gamma^{n-1}}2p^2\frac{\gamma}{(1+\gamma^2p^2)^2}\left(\frac{1+\xi\gamma}{\xi}\right)^n\right\}_{\gamma=0} \qquad \text{(B.1)}$$

where ξ is a constant, and retaining the first nonvanishing term in (B.1), we obtain

$$\mathcal{I}_1(\gamma_k\varkappa) = \left(\frac{\xi_k\gamma_k}{1+\xi_k\gamma_k}\right)^2 + \ldots, \quad \xi_k^2 = \frac{1}{4}\frac{\varkappa}{\varkappa^2+1/2\varkappa+3/8};$$

$$\mathcal{I}_2(\gamma_a\varkappa) = \left(\frac{\xi_a\gamma_a}{1+\xi_a\gamma_a}\right)^2 + \ldots \qquad \text{(B.2)}$$

$$\xi_a^2 = (\varkappa-1)^{-2}\left[\varkappa^2+2\varkappa-3\varkappa\left(\frac{\varkappa}{\varkappa-1}\right)^{1/2}\ln[(\varkappa-1)^{1/2}+\varkappa^{1/2}]\right].$$

This result gives the asymptotic behavior in γ because the accuracy that can be achieved by including the next terms in (B.1) increases only for sufficiently large γ. However, comparison with numerical calculations performed on a computer has shown that one can confine one's attention to the first terms for the entire range of values of γ if the experimental range of uncertainty (~10%) is to be achieved in (B.2).

APPENDIX C

We shall now take into account the nondiagonal matrix element of the operator Ω in the evaluation of the matrix $K_{ss'}$. We have

$$\Delta\varkappa^{\parallel} = \Delta\varkappa_{kk}^{\parallel} + \Delta\varkappa_{aa}^{\parallel} + \Delta\varkappa_{ka}^{\parallel} + \Delta\varkappa_{ak}^{\parallel}, \qquad \text{(C.1)}$$

where the last two terms contain the nondiagonal elements K_{ka} and K_{ak},

$$\Delta\varkappa_{ka}^{\parallel} = \frac{4\pi}{3}\langle\nu_k|\Omega_1|0\rangle\langle\nu_a|\Omega_1|0\rangle\langle\nu_k|K|\nu_a\rangle, \qquad \text{(C.2)}$$

and the expression for $\Delta\varkappa_{ak}^{\parallel}$ differs by the sign and the replacement of k with a. Using (2.3) in (C.2), we obtain

$$\Delta\varkappa_{ka}^{\parallel} = \frac{4\pi}{3}\Omega_{k0}\Omega_{a0}\sum_{h_1'h_2'h_1h_2}\langle 1h_1'2h_2'|10\rangle\langle 2h_11h_2|10\rangle\langle\nu_k|K|\nu_a\rangle. \qquad \text{(C.3)}$$

We now take the set of vectors $|s\rangle$ as the basis for the operator H. We then have

$$H|s\rangle = H_{ss}|s\rangle + \sum_{s'\neq s}H_{s's}|s'\rangle.$$

The function F will now be chosen so that

$$H_{s's}|s'\rangle = \theta_{s's}F|s\rangle, \quad \theta_{s's} = \frac{H_{s's}}{F_{s's}},$$

$$H_{ss}|s\rangle = [H_{ss}^{(0)} + \theta_sF]|s\rangle, \quad \theta_s = \frac{H_{ss}-H_{ss}^{(0)}}{F_{ss}} \qquad \text{(C.4)}$$

where $H^{(0)}$ is the diagonal part of H. From (C.4), we then have

$$H|s\rangle=[H^{(0)}_{ss}+\bar{\theta}_s F]|s\rangle, \quad \bar{\theta}_s=\theta_s+\sum_{s'}\theta_{s's}. \tag{C.5}$$

This result readily yields the formal expression for the matrix elements of the operator H^{-1}:

$$\langle s|H^{-1}|s'\rangle=\langle s|(H^{(0)}_{ss}+\bar{\theta}_s F)^{-1}|s'\rangle. \tag{C.6}$$

From this, we obtain

$$\operatorname{Re}\langle \nu_k|K|\nu_a\rangle=-\frac{1}{\Omega^{(0)}_k}\left\langle \nu_k \left| \frac{(\gamma_k h_2' x/J)^2}{(1+Z_k F)^2+(\gamma_k h_2' x/J)^2}\,\frac{1}{1+Z_k F}\right| \nu_a\right\rangle, \quad Z_k=\frac{\bar{\theta}_k}{\Omega^{(0)}_k}. \tag{C.7}$$

Using the Bürmann expansion (B.1) in (C.7), we have

$$\operatorname{Re}\langle \nu_k|K|\nu_a\rangle=-\frac{1}{\Omega^{(0)}_k}\left[\frac{\pi_k\gamma_k}{1+\pi_k\gamma_k}\right]^2 \pi_k^{-2}\langle \nu_k|\left(\frac{x}{J}h_2'\right)^2(1+Z_k F)^{-1}|\nu_a\rangle. \tag{C.8}$$

The coefficient π_k in (C.8) can be found with the aid of (C.7) by allowing γ_k to tend to infinity:

$$\pi_k^2=\frac{\langle \nu_k|(x/Jh_2')^2(1+Z_k F)^{-1}|\nu_a\rangle}{\langle \nu_k|(1+Z_k F)^{-1}|\nu_a\rangle}\approx\langle \nu_k|\left[\frac{x}{J}h_2'\right]^2|\nu_k\rangle, \tag{C.9}$$

where, in the expression for π_k, we have neglected the nondiagonal elements of the operator $(xh_2'/J)^2$. When (C.6), (C.8), and (C.9) are taken into account, the final expression assumes the following form:

$$\operatorname{Re}\langle \nu_k|K|\nu_a\rangle=-\langle \nu_k|\Omega^{-1}|\nu_a\rangle\left[\frac{\pi_k\gamma_k}{1+\pi_k\gamma_k}\right]^2. \tag{C.10}$$

We note that, in accordance with this result, the field dependence of the nondiagonal elements K_{ka} and K_{ak} is the same as the analogous dependence for the diagonal elements K_{kk} and K_{aa}.

[1)] We have introduced the dimensionless velocity $\mathbf{c}=(m/2T)^{1/2}\mathbf{u}$, where m is the mass of the molecule and T is the temperature.

[2)] As in the paper by Kagan and Maksimov,[20] we have introduced the spherical system of coordinates.

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