Senftleben-Beenakker Effects, Nonresonant Absorption and Collision Integrals for Gases Consisting of Symmetric Top Molecules

H. Moraal

Institut für theoretische Physik, Universität zu Köln

(Z. Naturforsch. **29 a**, 299—305 [1974] ; received August 21, 1973)

The kinetic theories of the electric and magnetic Senftleben-Beenakker effects and of nonresonant absorption in polar symmetric top gases are reviewed, using an expansion of the distribution function-density matrix which includes the dipole moment operator $\boldsymbol{\mu}_e$. General expressions are given for the elastic parts of all collision integrals coupling two purely angular momentum dependent tensors. This is done for a variety of nonspherical potentials, including the dipole-dipole (DD), dipole-quadrupole (DQ) and quadrupole-quadrupole (QQ) interactions. Model calculations for the methyl halogenides are performed for these potentials for a number of collision integrals, namely the nonresonant cross section and three collision cross sections which are of importance for the shear viscosity Senftleben-Beenakker effects. These calculations indicate that DD, DQ and QQ interactions may all be important, that at least half of the nonresonant cross section is elastic and that the average cross section extracted by means of Levi's theory from electric field shear viscosity Senftleben-Beenakker measurements is approximately equal to the reorientation cross section for the tensor polarization $[\boldsymbol{\mu}_e]^{(2)}$.

1. Introduction

The kinetic theory of diatomic gases has been checked extensively against experiment and is found to be in excellent agreement with it. This makes it possible to give a very precise interpretation of the cross sections extracted from the experiments, which may then in turn be calculated from the intermolecular (nonspherical) potential. In this sense the theory of diatomic gases is complete and suffers only from a lack of data on nonspherical potentials and from the (largely computational) difficulties of collision integral calculations. The latter problem has, however, recently been extensively studied with very reasonable results [1–8].

For symmetric top gases, the situation is much more complicated. Due to the form of the internal state Hamiltonian of such molecules in the presence of an external electric field, infinitely many expansion tensors have to be used in order to give a reasonably accurate description of the electric field Senftleben-Beenakker (SB) effects [9–11]. The same is true for the magnetic field SB effects if the gyromagnetic tensor of the molecules is strongly anisotropic. This is the rule for symmetric top molecules rather than the exception. The same problem is encountered in the theory of pressure broadening [12]. A more precise statement of these difficulties is given in Section 2.

The theoretical difficulties mentioned above make it impossible to interpret the cross sections derived from experiment in a precise way. Instead, some average of an infinite number of collision cross sections is experimentally obtained and this average may be different for different molecules since it depends sensitively on the types of nonsphericity which are dominant. Therefore, in this article a number of cross sections which may be close to the average are calculated and the choice is made on the basis of a comparison.

The plan of the present article is the following. In Section 2 the existing theories of the SB effects and of pressure broadening are reviewed. An expansion of the distribution function-density matrix which differs slightly from the one used in the literature is employed. This expansion contains (before diagonalization in internal energy) the full dipole moment operator in addition to the rotational angular momentum operator as internal state variables.

In Section 3 the interaction between two (asymmetric top) molecules is briefly discussed and it is shown how this interaction may be simplified for prolate symmetric top molecules. General expressions for all angular momentum space collision cross sections which may be needed for the theories described in Section 2 are derived in the distorted wave Born approximation (DWBA) for elastic collisions. Special consideration is given to the relatively long range dipole-dipole (DD), dipole-quadrupole (DQ) and quadrupole-quadrupole (QQ) forces, since these can be calculated relatively easily [7].

Reprint requests to Dr. H. Moraal, Institut für theroretische Physik, Universität Köln, *D-5000 Köln 41*, Germany.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

In Section 4 such evaluations are done for a number of reorientation cross sections for the methyl halogenides CH_3F, CH_3Cl, CH_3Br and CH_3I. The results obtained are compared with the relevant experimental data and a discussion is given.

2. Kinetic Theory

In the theories of the shear viscosity SB effects and of pressure broadening an expansion of the distribution function-density matrix in purely internal state variable dependent tensors is needed. In the case of diatomic, or, more generally, linear diamagnetic molecules, the only quantity of importance is the angular momentum operator $\boldsymbol{J}$ — taken here as a dimensionless vector operator: $J^2 = j(j+1)$. For symmetric top molecules, however, there is a further quantum number k, the eigenvalue of the projection of $\boldsymbol{J}$ on the figure axis, J_Z. This quantity has now to be taken into account in some way. In Ref. 10 this was accomplished by taking into account the tensors $J_Z[\boldsymbol{J}]^{(q)}$ in addition to the tensors $[\boldsymbol{J}]^{(q)}$. This set was then completed by a complete set of energy polynomials.

It seems more natural, however, to include the complete (dimensionless) dipole moment operator $\boldsymbol{\mu}_e$ in the expansion, i. e., to consider all tensors of the form [$\mathbf{T}(p,k,l)$ is a Cartesian (3-j)-tensor]

$$\mathbf{T}(p,k,l) \odot^{k+l} [\boldsymbol{\mu}_e]^{(k)} [\boldsymbol{J}]^{(l)} \tag{1}$$

with, in order to have only Hermitean operators present after diagonalization, $p+k+l=$ even. Since the Waldmann-Snider equation is to be used, which is diagonal in internal energy eigenstates, Equation (1) has to be diagonalized. This may be accomplished by means of the equations

$$[\boldsymbol{\mu}_e]^{(k)} \text{ diag.} = \alpha_k [\boldsymbol{J}]^{(k)}, \tag{2}$$

$$\alpha_k = [\boldsymbol{\mu}_e]^{(k)} \odot^k [\boldsymbol{J}]^{(k)} \left([\boldsymbol{J}]^{(k)} \odot^k [\boldsymbol{J}]^{(k)} \right)^{-1}. \tag{3}$$

The first few tensors of the form (1) are given, together with their diagonal parts, in Table 1. Since the dimensionless vector $\boldsymbol{\mu}_e$ is equal to the unit vector $\boldsymbol{u}$ along the symmetry axis apart from the sign (which is unimportant), Equation (3) may easily be evaluated explicitly. The α_k occurring in Table 1 are listed in Table 3. After these preliminaries, a review of the existing theories of pressure broadening and of the SB effects can now be given.

Table 1. Some of the expansion tensors $\mathbf{T}(p,k,l) \odot^{k+l} [\boldsymbol{\mu}_e]^{(k)} [\boldsymbol{J}]^{(l)}$.

p	k	l	Tensor	Diagonal part
1	0	1	$\boldsymbol{J}$	$\boldsymbol{J}$
1	1	0	$\boldsymbol{\mu}_e$	$\alpha_1 \, , \boldsymbol{J}$
1	1	2	$\boldsymbol{\mu}_e \cdot [\boldsymbol{J}]^{(2)}$	$\frac{2}{3} \alpha_1 (J^2 - \frac{3}{4}) \boldsymbol{J}$
1	2	1	$[\boldsymbol{\mu}_e]^{(2)} \cdot \boldsymbol{J}$	$\frac{2}{3} \alpha_2 (J^2 - \frac{3}{4}) \boldsymbol{J}$
2	0	2	$[\boldsymbol{J}]^{(2)}$	$[\boldsymbol{J}]^{(2)}$
2	1	1	$[\boldsymbol{\mu}_e \boldsymbol{J}]^{(2)}$	$\alpha_1 [\boldsymbol{J}]^{(2)}$
2	2	0	$[\boldsymbol{\mu}_e]^{(2)}$	$\alpha_2 [\boldsymbol{J}]^{(2)}$
2	1	3	$\boldsymbol{\mu}_e \cdot [\boldsymbol{J}]^{(3)}$	$\frac{3}{5} \alpha_1 (J^2 - 2) [\boldsymbol{J}]^{(2)}$
2	3	1	$[\boldsymbol{\mu}_e]^{(3)} \cdot \boldsymbol{J}$	$\frac{3}{5} \alpha_3 (J^2 - 2) [\boldsymbol{J}]^{(2)}$

a) Pressure broadening

Tip and McCourt[12] derived a Chapman-Enskog-like equation for a function $\mathbf{G}(\omega)$ which is directly related to the absorption coefficient. For the case of nonresonant absorption this equation has the form

$$\alpha_1 \boldsymbol{J} = (i\omega - n\,\mathfrak{R})\,\mathbf{G}(\omega). \tag{4}$$

Here $\mathfrak{R}$ is the positive-semidefinite, density-independent Waldmann-Snider collision superoperator. If $\alpha_1 \boldsymbol{J}$ is an approximate eigenfunction of $\mathfrak{R}$, which does seem to be a reasonable assumption for moderately and strongly polar molecules, then the nonresonant cross section is given by

$$\sigma_{\text{nonres.}} = (\alpha_1 \boldsymbol{J}., \mathfrak{R}\,\alpha_1 \boldsymbol{J}) \langle \alpha_1^2 \boldsymbol{J}^2 \rangle_0^{-1} \langle v_{\text{rel}} \rangle_0^{-1}, \tag{5}$$

with $\langle v_{\text{rel}} \rangle_0 = (16\,k\,T/\pi\,m)^{1/2}$ and the inner product defined by (A, C and P velocity independent)

$$(A, C) = \langle A^+ C \rangle_0, \tag{6}$$

$$\langle P \rangle_0 = Q^{-1} \sum_{j=0}^{\infty} (2j+1) \exp[-B\,j(j+1)] \cdot \left\{ \sum_{k=-j}^{+j} P(J^2, k) \exp[-B(x-1)k^2] \right\}, \tag{6}$$

$$Q = \sum_{j=0}^{\infty} (2j+1) \exp[-B\,j(j+1)] \cdot \left\{ \sum_{k=-j}^{+j} \exp[-B(x-1)k^2] \right\}, \tag{7}$$

where B and x are given by

$$B = \hbar^2 (2\,I_A\,k\,T)^{-1}; \quad x = I_A / I_C \tag{8}$$

with I_A and I_C the moments of inertia (I_C around the symmetry axis) of the molecule.

For the description of the broadening of lines due to transitions within a Zeeman multiplet, the following field term has to be added to the right hand side of Equation (4):

$$i\,\mu_N\,\hbar^{-1} H [\hat{\mathbf{H}} \cdot \mathbf{g} \cdot \mathbf{J}, \mathbf{G}(\omega)]_-, \tag{9}$$

with μ_{N} the nuclear magneton, H the magnetic field strength, $\hat{\boldsymbol{H}}$ the field direction and $\mathbf{g}$ the rotational g-tensor. This tensor may be written as

$$\mathbf{g} = \tfrac{1}{3}(g_{\parallel} + 2\,g_{\perp})\,\mathbf{U} + (g_{\parallel} - g_{\perp})\,[\boldsymbol{u}]^{(2)} . \quad (10)$$

If this is diagonalized in internal energy using Equation (3), the result

$$\boldsymbol{H}\cdot\mathbf{g}\cdot\boldsymbol{J} = [g_{\perp} + (g_{\parallel} - g_{\perp})\,J_{\mathrm{Z}}^{2}\,J^{-2}]\,\boldsymbol{H}\cdot\boldsymbol{J} \quad (11)$$

is obtained. It is obvious that a field operator of this form will strongly couple different expansion tensors of an expansion of $\mathbf{G}(\omega)$, e.g., the $(p, k, l) = (1, 1, 0)$ and $(1, 1, 2)$ tensors of Table 1, so that for a complete description infinitely many tensors are needed, even if they are all eigenfunctions of $\Re$.

In Ref. 12, $\mathbf{G}(\omega)$ was approximated by a tensorial multiple of $\alpha_1 \boldsymbol{J}$. If this is a valid approximation, the cross section for Zeeman broadening, σ_{Zeeman}, is identical with $\sigma_{\mathrm{nonres.}}$. It may be expected that for large values of the anisotropy deviations from this equality occur and that the measured cross section is an average of the diagonal cross sections which may be constructed from the expansion tensors (1) with $p = 1$. For prolate symmetric top molecules, for which the ratio $k^2/j(j+1)$ is small in the most populated states at ordinary temperatures, replacement of Eq. (11) by its average,

$$\overline{g} = g_{\perp} + (g_{\parallel} - g_{\perp})\,\langle J_{\mathrm{Z}}^{2}\,J^{-2}\rangle_{0} , \quad (12)$$

may not be too bad an approximation, however. In that case σ_{Zeeman} and $\sigma_{\mathrm{nonres.}}$ may be approximately equal.

For the broadening of lines caused by transitions within a Stark multiplet, Equation (4) must be replaced by [12] (the field term is already diagonalized)

$$a_1 \boldsymbol{J} = (i\,\omega - n\,\Re)\,\mathbf{G}(\omega) + i\,\mu_{\mathrm{e}}\,\hbar^{-1}\,E\,[\hat{\boldsymbol{E}}\cdot a_1 \boldsymbol{J}, \mathbf{G}(\omega)]_{-} . \quad (13)$$

Here a strong coupling between different expansion tensors is induced by the field term while there are no diagonal "field brackets" as in the Zeeman case. Therefore, an average cross section is certainly observed here. It has been argued [12] that this average is, in fact, not too much different from $\sigma_{\mathrm{nonres.}}$. Whether or not this is true can only be ascertained by means of the same type of calculations as presented in this article for the shear viscosity SB effect.

b) Shear viscosity SB effects

As is well-known, the shear viscosity SB effects may be obtained upon solving the Chapman-Enskog equation [13] (magnetic field case)

$$2[\boldsymbol{W}]^{(2)} = n\,\Re\,\mathbf{B} - i\,\mu_{\mathrm{N}}\,\hbar^{-1}\,H[\hat{\boldsymbol{H}}\cdot\mathbf{g}\cdot\boldsymbol{J}, \mathbf{B}]_{-} \quad (14)$$

for the second rank symmetric traceless tensor $\mathbf{B}$. Again it may be expected that in Eq. (14) an average g-factor may be used, especially for prolate symmetric tops. If this is the case, then if one of the tensors $(p = 2)$ of Eq. (1) is most strongly coupled to $[\boldsymbol{W}]^{(2)}$ by the collision superoperator, the same shape of the SB curves as obtained for linear molecules may be expected. Experimentally, this has only been verified for the thermal conductivity of the oblate molecule NF_3 [14].

The question then still remains which tensor this is, $[\boldsymbol{J}]^{(2)}$ as in the case of linear molecules or another tensor. The calculations in Section 4 indicate that the diagonal $[\boldsymbol{J}]^{(2)}$ cross section is relatively small, while the diagonal $[\boldsymbol{\mu}_{\mathrm{e}}]^{(2)}$ cross section is about two orders of magnitude larger, at least for the methyl halogenides. Therefore, an experimental method for deciding the above question is very simple, consisting only in a measurement of the SB effect and a calculation of the cross section determining the half-value $(H/p)_{1/2}$ using the average g-factor given by Equation (12). Experimental clarification is needed here since calculations of the inelastic collision integrals coupling $[\boldsymbol{W}]^{(2)}$ to a second rank angular momentum dependent tensor are prohibitively difficult for symmetric top molecules. Such calculations can, moreover, hardly be performed with any accuracy before many more data on the short range nonspherical interaction between two symmetric top molecules are available. Such data seem to be practically nonexistent at present.

For the electric field SB effects, the field term in Eq. (14) has to be replaced by the one occurring in Equation (13). For this case, Levi derived an approximate expression for the SB effects under the assumption that the collision superoperator may be replaced by a constant [11]. This theory of Levi is the quantum mechanical analogue of the classical theory of Mikhaĭlova and Maksimov [9], i.e., it is essentially a perturbation type of solution, although Levi proved that the usual variational type of solution gives the same result if infinitely many expansion tensors are taken into account[11]. Using a splitting of the collision operator in zeroth and first order parts which is superior to the one used in Reference 9, Levi could describe the shear viscosity SB effects in terms of the function

$$f_{02}(\xi_{02},x)=\langle J^2(J^2-\tfrac{3}{4})\,\alpha_1{}^2\,\xi_{02}{}^2\,(B+\alpha_1{}^2\,\xi_{02}{}^2)^{-1}\rangle_0 \times\langle J^2(J^2-\tfrac{3}{4})\rangle_0{}^{-1} \qquad (15)$$

with ξ_{02} given by

$$\xi_{02}=\mu_e\,E\,B^{1/2}(n\,\hbar\,\sigma_{SB}\,\langle v_{rel}\rangle_0)^{-1}, \qquad (16)$$

where σ_{SB} is the effective average cross section. Equation (15) fits the experimental data excellently[11]. It will be shown in Section 4 that at least for the prolate methyl halogenides the average cross section derived from the experiments using Levi's theory is close to the diagonal cross section associated with $[\boldsymbol{\mu}_e]^{(2)}$ and certainly not equal to the diagonal cross section associated with $[\boldsymbol{J}]^{(2)}$ as originally proposed by Levi[11].

It might be asked whether it is not possible to derive more exact expressions for the SB effects and the pressure broadening cross sections. The answer is: in principle, yes, in practice, no. This is easily seen by considering what would have to be done for a complete description: for at least one type of nonspherical potential all collision integrals for a basis in angular momentum space (of total rank one or two) have to be evaluated together with all "field brackets". Formally, this is not too difficult, but in order to do a calculation for a particular gas these have all to be done numerically and for every gas again! Then the so-obtained set of equations would have to be solved, again numerically; but this is clearly impossible since all equations are needed to describe the approach to saturation of the SB effects, for example. It is therefore not to be expected that the kinetic theory of symmetric top gases will ever yield as much useful information as the kinetic theory of linear molecules.

3. Collision Integrals

In order to evaluate collision integrals, a description of the intermolecular potential is necessary. The orientation in space of any rigid molecule may be given in terms of the orientations of two unit vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ attached to the molecular framework such that $\boldsymbol{u}\cdot\boldsymbol{v}=0$. The most general orientation dependent potential is then of the form $(\boldsymbol{u}_1\cdot\boldsymbol{v}_1=\boldsymbol{u}_2\cdot\boldsymbol{v}_2=0)$

$$\begin{aligned}V(\boldsymbol{u}_1,\boldsymbol{u}_2,\boldsymbol{v}_1,\boldsymbol{v}_2,\mathbf{R}) &=\sum_{L,N,P}\Big\{\sum_{l_1,l_2}[\boldsymbol{u}_1]^{(l_1)}\,[\boldsymbol{u}_2]^{(l_2)}\odot^{l_1+l_2}\mathbf{T}(l_1,l_2,L)\Big\}\\ &\cdot\Big\{\sum_{n_1,n_2}[\boldsymbol{v}_1]^{(n_1)}[\boldsymbol{v}_2]^{(n_2)}\odot^{n_1+n_2}\mathbf{T}(n_1,n_2,N)\Big\} \qquad (17)\\ &\cdot\odot^{L+N}\mathbf{T}(L,N,P)\odot^{P}[\hat{\mathbf{R}}]^{(P)}\,V_{l_1l_2L,n_1n_2N,P}(R)\,.\end{aligned}$$

Here $\boldsymbol{R}$ (magnitude R, direction $\hat{\mathbf{R}}$) is the vector extending from the center-of-mass of molecule 1 to the center-of-mass of molecule 2. It should be noted that the order in which the Clebsch-Gordan "additions" have been performed in Eq. (17) is arbitrary. The special order adopted here is the most advantageous for the purposes of this article.

For linear molecules, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ may be chosen along the internuclear axes of the molecules. Due to the C_∞ symmetry around these axes, the only values allowed for n_1 and n_2 are then zero, so that $N=0$ and, consequently, $P=L$. Equation (17) then reduces to the form used earlier[5, 7] for such molecules.

For symmetric top molecules, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are chosen along the figure axes of the molecules. Since these are at least threefold symmetry axes, the lowest value that n_1 and n_2 can take which yields tensors that are not expressible in terms of $\boldsymbol{u}_1$, respectively $\boldsymbol{u}_2$, is 3. Therefore, if interest is focused on the lowest rank contributions, Equation (17) may approximately be replaced by

$$\begin{aligned}V(\boldsymbol{u}_1,\boldsymbol{u}_2,\boldsymbol{v}_1,\boldsymbol{v}_2,\mathbf{R})&\cong V(\boldsymbol{u}_1,\boldsymbol{u}_2,\mathbf{R})\\ &=\sum_{l_1<3,\,l_2<3,\,L<5}[\boldsymbol{u}_1]^{(l_1)}[\boldsymbol{u}_2]^{(l_2)}\odot^{l_1+l_2} \qquad (18)\\ &\quad\cdot\mathbf{T}(l_1,l_2,L)\odot^{L}[\mathbf{R}]^{(L)}\,V_{l_1l_2L}(R)\,,\end{aligned}$$

which is identical with the lower order result for linear molecules. Equation (18) will be applicable in particular to prolate symmetric top molecules. For oblate tops third and higher rank tensors may be assumed to be of importance as well. It should be stressed that Eq. (18) contains the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions exactly, for all kinds of symmetric top molecules. For spherical tops, Equation (18) gives a zero result: for such molecules the intermolecular potential contains third or fourth rank tensors in lowest order.

Equation (18) may be diagonalized in internal energy if the effect of elastic collisions only is required. This approximation is consistent with the use of the Waldmann-Snider equation in the electric and (anisotropic g-tensor!) magnetic field effects: since this equation is diagonal in internal energy, the dipole moment operator and the quadrupole moment operator have already been diagonalized in the field commutators. Therefore, the same should be done in Equation (18). In the following equations the diagonalized potentials for which collision integrals are calculated in this article are listed together with their names.

a) Single-P_1 potential (P_1), $(l_1\, l_2\, L) = (101)$ and (011):

$$V(P_1) = V_{101}(R)\,[\alpha_1(1)\boldsymbol{J}_1 - \alpha_1(2)\boldsymbol{J}_2]\cdot\hat{\boldsymbol{R}}\,. \quad (19)$$

b) Single-P_2 potential (P_2), $(l_1\, l_2\, L) = (202)$ and (022):

$$V(P_2) = V_{202}(R)[\alpha_2(1)\,[\boldsymbol{J}_1]^{(2)} + \alpha_2(2)\,[\boldsymbol{J}_2]^{(2)}]:[\hat{\boldsymbol{R}}]^{(2)}\,. \quad (20)$$

c) Dipole-dipole interaction (DD), $(l_1\, l_2\, L) = (112)$:

$$V(\mathrm{DD}) = 3\,\mu_e^2 R^{-3}\alpha_1(1)\,\alpha_1(2)\boldsymbol{J}_1\boldsymbol{J}_2:[\hat{\boldsymbol{R}}]^{(2)}\,. \quad (21)$$

d) Dipole-quadrupole interaction (DQ), $(l_1\, l_2\, L) = (123)$ and (213):

$$V(\mathrm{DQ}) = \tfrac{15}{4}\,\mu_e Q_e R^{-4}\{\alpha_2(1)\,\alpha_1(2)\,[\boldsymbol{J}_1]^{(2)}\boldsymbol{J}_2 - \alpha_1(1)\,\alpha_2(2)\boldsymbol{J}_1[\boldsymbol{J}_2]^{(2)}\}\odot^3[\hat{\boldsymbol{R}}]^{(3)}\,. \quad (22)$$

e) Quadrupole-quadrupole interaction (QQ), $(l_1\, l_2\, L) = (224)$:

$$V(\mathrm{QQ}) = \tfrac{105}{4}\,Q_e^2 R^{-5}\alpha_2(1)\,\alpha_2(2)\cdot[\boldsymbol{J}_1]^{(2)}[\boldsymbol{J}_2]^{(2)}\odot^4[\hat{\boldsymbol{R}}]^{(4)}\,. \quad (23)$$

In these equations μ_e and Q_e are the scalar values of the electric dipole and quadrupole moments, respectively, while $\alpha_k(\mathrm{i})$ is α_k for molecule i.

For a calculation of collision integrals, the transition operator matrix elements $t(\boldsymbol{g},\boldsymbol{g}')$ between relative velocity eigenstates are needed. In the distorted wave Born approximation the transition operator corresponding to the potential (18) is [1–7] (since the nonspherical part of the potential is of interest here, the set of indices (000) should be omitted)

$$t(\boldsymbol{g},\boldsymbol{g}') = \sum_{l_1<3,\, l_2<3,\, L<5}[\boldsymbol{u}_1]^{(l_1)}[\boldsymbol{u}_2]^{(l_2)}\odot^{l_1+l_2}\mathbf{T}(l_1,l_2,L)\times\odot^L\mathbf{A}^{(L)}_{l_1 l_2}(\boldsymbol{g},\boldsymbol{g}') \quad (24)$$

with

$$\mathbf{A}^{(L)}_{l_1 l_2}(g,g') = \langle\boldsymbol{g}\,|\,V_{l_1 l_2 L}(R)\;[\mathbf{R}]^{(L)}|\,\boldsymbol{g}'\rangle \quad (25)$$

where $|\,\boldsymbol{g}\rangle$ is the scattering wave function for the relative velocity $\boldsymbol{g}$ corresponding to the spherical part $V_0(R) = V_{000}(R)$ of the potential. For more details, see Reference 7.

Exactly as in the case of linear molecules, the cross sections (for elastic collisions) corresponding to the collision integrals coupling two purely angular momentum dependent functions $f(J_Z, J^2)\,[\boldsymbol{J}]^{(q)}$ and $g(J_Z, J^2)\,[\boldsymbol{J}]^{(q)}$ may now be shown to be given by

$$\begin{aligned}\sigma_q\{f,g\} &= (f[\boldsymbol{J}]^{(q)}\odot^q, \Re\, g[\boldsymbol{J}]^{(q)})\cdot(f,g\,|\,q)_0^{-1}\langle v_{\mathrm{rel}}\rangle_0^{-1}\\ &= (2\pi)^4\hbar^2(f,g\,|\,q)_0^{-1}\langle v_{\mathrm{rel}}\rangle_0^{-1}\,\mathrm{tr}_1\,\mathrm{tr}_2\iiiint f_1^{(0)} f_2^{(0)}\\ &\quad f(1)\,[\boldsymbol{J}_1]^{(q)}\odot^q[g(1)\,[\boldsymbol{J}_1]^{(q)} + g(2)\,[\boldsymbol{J}_2]^{(q)}, t(\boldsymbol{g},\boldsymbol{g}')]_-\\ &\quad t^\dagger(\boldsymbol{g},\boldsymbol{g}')\,\delta(E)\,\delta(\boldsymbol{P})\,\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2\,\mathrm{d}\boldsymbol{p}_1'\,\mathrm{d}\boldsymbol{p}_2'\,. \end{aligned} \quad (26)$$

Here

$$f^{(0)} = (2\pi m k T)^{-3/2}\exp(-W^2)Q^{-1}\exp\{-B[J^2 + (x-1)\,J_Z^2]\} \quad (27)$$

is the equilibrium distribution function-density matrix, the symbol tr indicates that a trace over internal degrees of freedom is to be taken (including summation over j and k) and the Dirac delta functions express energy and momentum conservation. The "inner product" $(f,g\,|\,q)_0$ is defined in Table 3 [§].

Upon insertion of the transition operator associated with the potentials (19 – 23) and evaluation of the traces, the expressions listed in Table 2 are obtained. (For the methods used in the trace evaluations, see Appendix C of Reference 5.) In Table 2,

Table 2. Elastic collision integrals $\sigma_q\{f,g\}$ for several types on nonsphericity.

Potential	l_1	l_2	L	$\dfrac{\sigma_q'\{f,g\}(f,g\,\|\,q)_0}{\sigma l_1 l_2 L(0)}$	$\dfrac{\sigma_q''\{f,g\}(f,g\,\|\,q)_0}{\sigma l_1 l_2 L(0)}$
P_1	1 0	0 1	1 1	$\frac{1}{2}\,q(q+1)\,(f\,g\,\|\,q)_1$	0
P_2	2 0	0 2	2 2	$\frac{9}{4}\,q(q+1)\,(f\,g\,\|\,q)_2$	0
DD	1	1	2	$\frac{5}{18}\,q(q+1)\,(f\,g\,\|\,q)_1\,(1\,\|\,1)_1$	$q=1$: $\frac{5}{18}(f\,\|\,1)_1(g\,\|\,1)_1$
DQ	1 2	2 1	3 3	$\frac{7}{20}q(q+1)\,\{(f\,g\,\|\,q)_1(1\,\|\,1)_2 + 3(f\,g\,\|\,q)_2(1\,\|\,1)_1\}$	$q=1$: $-\frac{7}{10}\{(f\,\|\,1)_2(g\,\|\,1)_1 + (f\,\|\,1)_1(g\,\|\,1)_2\}$ $q=2$: $-\frac{14}{25}(f\,\alpha_2/\alpha_1\,\|\,2)_1 \times (g\,\alpha_2/\alpha_1\,\|\,2)_1$ $q=3$.
QQ	2	2	4	$\frac{243}{100}q(q+1)\,(f\,g\,\|\,q)_2\,(1\,\|\,1)_2$	$q=1$: $\frac{81}{50}(f\,\|\,1)_2(g\,\|\,1)_2$ $q=3$.

[§] Note that $(f,g\,|\,q)_0$ does not define a real inner product since it is nonlinear: in general, $(f+h,g\,|\,q)_0 \neq (f,g\,|\,q)_0 + (h,g\,|\,q)_0$, although $(\mu f,g\,|\,q)_0 = \mu(f,g\,|\,q)_0$. The Schwartz inequality is an equality for this "inner product".

the cross sections are split in two parts

$$\sigma_q\{f,g\} = \sigma_q'\{f,g\} + \sigma_q''\{f,g\}, \tag{28}$$

the first one coming from the term with $g(1)$ as a factor, the second one from the term with $g(2)$. Those values of q for which $\sigma_{q''}\{f,g\}$ is nonzero are also given in Table 2 together with the nonzero $\sigma_{q''}\{f,g\}$ for $q \leqq 2$, the $q=3$ collision integrals being of no importance for the effects considered in the previous section.

The cross sections $\sigma_{l_1 l_2 L}(0)$ are defined by

$$\sigma_{l_1 l_2 L}(0) = (2\pi)^4 \hbar^2 (2L+1)^{-1} \langle v_{\mathrm{rel}}\rangle_0{}^{-1} \cdot \iiiint h_1{}^{(0)} h_2{}^{(0)} \mathbf{A}_{l_1 l_2}^{(L)}(\boldsymbol{g},\boldsymbol{g}') \odot^L \mathbf{A}_{l_1 l_2}^{(L)*}(\boldsymbol{g},\boldsymbol{g}')\, \delta(E)\, \delta(\boldsymbol{P})\, \mathrm{d}\boldsymbol{p}_1\, \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_1{}'\, \mathrm{d}\boldsymbol{p}_2{}', \tag{29}$$

where the δ-function in energy now selects those collisions which are elastic, i. e., for which $g^2 = g'^2$. The function $h^{(0)}$ is the translational part of $f^{(0)}$. For the special cases of the multipole-multipole interactions, $\sigma_{l_1 l_2 L}(0)$ may be approximated by making use of a model described in Reference 7. The results of such an approximation (for large mass, see Appendix B of Ref. 7) are given in Table 3 together with the different averages occurring in Table 2, $(h\,|\,q)_1$ and $(h\,|\,q)_2$. The length d occurring in the $\sigma_{l_1 l_2 L}(0)$ expressions is chosen in such a way that the shear viscosity of the gas is given by [7, 8]

$$\eta_0 = \tfrac{5}{4} k T (\langle v_{\mathrm{rel}}\rangle_0 \pi d^2)^{-1}.$$

Table 3. Definitions of the quantities used in Tables 1 and 2.

Quantity	Explicit form
α_1	$J_Z J^{-2}$
α_2	$\frac{3}{2}(J_Z^2 - \frac{1}{3}J^2) J^{-2} (J^2 - \frac{3}{4})^{-1}$
α_3	$\frac{5}{2} J_Z (J_Z^2 - \frac{3}{5}J^2) J^{-2} (J^2 - \frac{3}{4})^{-1} (J^2 - 2)^{-1}$
$(h_1, h_2\,\|\,q)_0$	$\langle h_1{}^2 [\boldsymbol{J}]^{(q)} \odot^q [\boldsymbol{J}]^{(q)}\rangle_0{}^{1/2}$ $\langle h_2{}^2 [\boldsymbol{J}]^{(q)} \odot^q [\boldsymbol{J}]^{(q)}\rangle_0{}^{1/2}$
$(h\,\|\,q)_1$	$\langle \alpha_1{}^2 h [\boldsymbol{J}]^{(q)} \odot^q [\boldsymbol{J}]^{(q)}\rangle_0$
$(h\,\|\,q)_2$	$\frac{4}{9}\langle \alpha_2{}^2 h [J^2 - \frac{1}{4}(q^2+q+1)]$ $[\boldsymbol{J}]^{(q)} \odot^q [\boldsymbol{J}]^{(q)}\rangle_0$
$\sigma_{112}(0)$	$\frac{3}{5}\pi m \mu_e{}^4 (\hbar^2 k T d^2)^{-1}$
$\sigma_{123}(0) = \sigma_{213}(0)$	$\frac{15}{112}\pi m \mu_e{}^2 Q_e{}^2 (\hbar^2 k T d^4)^{-1}$ $= \frac{25}{112}\gamma\,\sigma_{112}(0);\ (Q_e/\mu_e d)^2 = \gamma$
$\sigma_{224}(0)$	$\frac{35}{24}\pi m Q_e{}^4 (\hbar^2 k T d^6)^{-1} = \frac{175}{72}\gamma^2 \sigma_{112}(0)$

4. Calculations for the Methyl Halogenides

The molecules selected for a calculation of the elastic multipole collision integrals are the methyl halogenides CH_3F, CH_3Cl, CH_3Br and CH_3I, because for these prolate molecules all molecular quantities needed (including the quadrupole moment [15]) are known and because nonresonant [16] and electric field SB data [11] (except for CH_3I) have been reported in the literature. The data necessary for the calculations are collected in Table 4 together with the derived quantities d^2 (from the shear viscosity), $\gamma = (Q_e/\mu_e d)^2$ and $B\,\sigma_{112}$.

The evaluation of the collision integrals of Table 2 is then reduced to the calculation of a number of averages of the form (6). This may be done in the classical limit, i. e., the sums are replaced by integrals and only the highest powers of j and k are taken into account. The results for $\sigma_1\{\alpha_1, \alpha_1\}$, $\sigma_2\{1,1\}$, $\sigma_2\{\alpha_1, \alpha_1\}$ and $\sigma_2\{\alpha_2, \alpha_2\}$, which are the diagonal cross sections for the tensor polarizations $J_Z \tau J^{-2} = \boldsymbol{\mu}_{\mathrm{e,\,diag.}}$, $[\boldsymbol{J}]^{(2)}$, $J_Z [\boldsymbol{J}]^{(2)} J^{-2} = [\boldsymbol{\mu}_e \boldsymbol{J}]^{(2)}_{\mathrm{diag}}$ and $\frac{3}{2}(J_Z{}^2 - \frac{1}{3}J^2)[\boldsymbol{J}]^{(2)} \times J^{-2}(J^2 - \frac{3}{4})^{-1} = [\boldsymbol{\mu}_e]^{(2)}_{\mathrm{diag.}}$, respectively, are given in Tables 5, 6 and 7.

In Table 5, the cross section $\sigma_1\{\alpha_1, \alpha_1\}$ is given, corresponding to reorientation of the dipole moment of the molecule, Equation (5). As expected, the di-

Table 5. The cross section $\sigma_1\{\alpha_1, \alpha_1\}$.

Molecule	$\sigma_1\{\alpha_1, \alpha_2\}$ (Å^2) DD	DQ	QQ	Total	$\sigma_{\mathrm{nonres.}}$ [a] (Å^2)
CH_3F	106	0.7	0	107	130
CH_3Cl	80	0.5	0	81	160
CH_3Br	84	4.9	3.0	92	190
CH_3I	70	10.5	19.1	100	230

[a] Reference 16.

Table 4. Molecular properties [a] and derived quantities for the methyl halogenides.

Molecule	Mass (10^{-22} g)	$B^{-1/2}$	x	μ_e (D)	Q_e (D. Å)	d^2 (Å^2)	γ	$B\,\sigma_{112}$ (Å^2)
CH_3F	0.57	15.4	6.0	1.86	−1.4	29.5	0.019	403
CH_3Cl	0.84	21.8	11.6	1.87	1.2	29.8	0.014	298
CH_3Br	1.58	25.4	16.0	1.80	3.6	34.3	0.116	308
CH_3I	2.36	27.2	20.8	1.65	5.4	37.4	0.288	259

[a] All data have been taken from the tables of Ref. 11 except for the Q_e values which are from Reference 15.

pole-dipole interaction gives the largest contribution to this collision integral, although DQ and QQ interactions are certainly not negligible for CH_3Br and CH_3I. A comparison of the calculated cross section with the experimental $\sigma_{\text{nonres.}}$ [16] shows agreement to within a factor of 2. Better agreement ist not to be expected since no short range P_1 and P_2 potentials nor higher order potentials could be calculated. Furthermore, all inelastic contributions to the cross sections have been neglected as well. That this becomes an increasingly worse approximation with increasing mass, as seen from Table 5, is due to the fact that the exchange of energy between rotational and translational degrees of freedom becomes easier as the moments of inertia of the molecule increase.

Table 6. DD, DQ and QQ contributions to $\sigma_2\{1, 1\}$, $\sigma_2\{\alpha_1, \alpha_1\}$ and $\sigma_2\{\alpha_2, \alpha_2\} \cdot (\text{Å}^2)$.

Molecule	$\sigma_2\{1, 1\}$			$\sigma_2\{\alpha_1, \alpha_1\}$			$\sigma_2\{\alpha_2, \alpha_2\}$		
	DD	DQ	QQ	DD	DQ	QQ	DD	DQ	QQ
CH_3F	3.6	0.1	0	65	0.4	0	125	1.5	0.3
CH_3Cl	1.0	0	0	37	0.2	0	58	0.5	0.1
CH_3Br	0.6	0.2	0.6	32	1.9	1.2	49	4.1	7.8
CH_3I	0.3	0.4	3.3	21	3.7	6.9	34	7.5	41

Table 7. The cross sections $\sigma_2\{1, 1\}$, $\sigma_2\{\alpha_1, \alpha_1\}$, $\sigma_2\{\alpha_2, \alpha_2\}$ and $\sigma_{\text{SB}} \cdot (\text{Å}^2)$.

Molecule	$\sigma_2\{1, 1\}$	$\sigma_2\{\alpha_1, \alpha_1\}$	$\sigma_2\{\alpha_2, \alpha_2\}$	σ_{SB} [a]
CH_3F	4	65	127	160
CH_3Cl	1	37	59	180
CH_3Br	1	35	61	230
CH_3I	4	32	83	—

[a] Reference 11.

In Table 6 the results for the reorientation cross sections of $[\boldsymbol{J}]^{(2)}$, $[\boldsymbol{\mu}_{\text{e}} \boldsymbol{J}]^{(2)}_{\text{diag.}}$ and $[\boldsymbol{\mu}_{\text{e}}]^{(2)}_{\text{diag.}}$ are assembled. Again DQ and QQ interactions are important for CH_3Br and CH_3I. The very large QQ contribution to $\sigma_2\{\alpha_2, \alpha_2\}$ for CH_3I is particularly interesting: it is due to the fact that $[\boldsymbol{\mu}_{\text{e}}]^{(2)}$ is proportional to the quadrupole tensor of the molecule. The total cross sections are given in Table 7 and are compared with σ_{SB}, the average cross section derived from the electric field SB effects [11] (Equation 16). As can be seen from the table, it would seem that σ_{SB} is approximately equal to $\sigma_2\{\alpha_2, \alpha_2\}$ and certainly not to $\sigma_2\{1, 1\}$ as assumed in Reference 11. As indicated in Section 2, statements like these are not necessarily valid for other molecules.

It may then be concluded that the approximate equalities

$$\sigma_{\text{nonres.}} \approx \sigma_1\{\alpha_1, \alpha_1\} \tag{30}$$

and

$$\sigma_{\text{SB}} \approx \sigma_2\{\alpha_2, \alpha_2\} \tag{31}$$

hold rather accurately for the methyl halogenides. Equation (30) confirms the theory of Tip and McCourt [12], while Ep. (31) indicates that for these prolate, moderately polar molecules the reorientation of the second tensor $[\boldsymbol{\mu}_{\text{e}}]^{(2)}$ is more important for the shear viscosity SB effects than $[\boldsymbol{J}]^{(2)}$, in contrast to nonpolar linear molecules where the latter tensor is all-important.

The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

---

[1] S. Hess and W. E. Köhler, Z. Naturforsch. **23 a**, 1903 [1968].

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

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

[4] W. E. Köhler, Z. Naturforsch. **28 a**, 815 [1973].

[5] F. M. Chen, H. Moraal, and R. F. Snider, J. Chem. Phys. **57**, 542 [1972].

[6] H. Moraal and R. F. Snider, Chem. Phys. Letters **9**, 401 [1971].

[7] H. Moraal, Z. Naturforsch. **28 a**, 824 [1973].

[8] H. MMoraal, Physica **60**, 64 [1973].

[9] Yu. V. Mikhailova and L. Maksimov, Soviet Phys. – JETP **24**, 1265 [1967].

[10] A. C. Levi, F. R. McCourt, and A. Tip, Physica **39**, 165 [1968].

[11] F. Tommassini, A. C. Levi, G. Scoles, J. J. de Groot, J. W. van den Broeke, C. J. N. van den Meijdenberg, and J. J. M. Beenakker, Physica **49**, 299 [1970].

[12] A. Tip and F. R. McCourt, Physica **52**, 109 [1971].

[13] H. Moraal and F. R. McCourt, J. Chem. Phys. **56**, 1588 [1972].

[14] J. J. de Groot, L. J. F. Hermans, C. J. N. van den Meijdenberg, and J. J. M. Beenakker, Phys. Letters **31 A**, 304 [1970].

[15] J. M. Pochan, R. L. Shoemaker, R. G. Stone, and W. H. Flygare, J. Chem. Phys. **52**, 2478 [1970].

[16] G. Birnbaum, J. Chem. Phys. **27**, 360 [1957].