

A COMPARISON OF DATA ON THE VISCOMAGNETIC EFFECT, FLOW BIREFRINGENCE AND DEPOLARIZED RAYLEIGH LINE BROADENING

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A comparison of data on the viscomagnetic effect, flow birefringence and depolarized Rayleigh line broadening for various gases of linear molecules at temperatures between 90 and 293 K is carried out. From the combined results information is obtained on the scalar structure of the non-equilibrium angular momentum polarization produced in viscous flow.

1. Introduction

The second rank angular momentum polarization is responsible for such seemingly unrelated phenomena as the viscomagnetic effect, flow birefringence and the collisional broadening of the depolarized Rayleigh line in dilute gases of linear molecules.

The first two effects are a consequence of the steady state non-equilibrium angular momentum polarization produced in viscous flow. While the tensorial structure of this polarization is known, the scalar factor (which depends on the magnitude of the reduced peculiar velocity W and/or the angular momentum operator J) has so far remained undetermined. As early as 1974 Hess¹⁾ pointed out that a comparison between the viscomagnetic effect and flow birefringence offers a possibility to obtain information on this scalar factor. Such a comparison will be carried out in section 2.

The third effect is caused by collisional decay of a second rank in J polarization, which is temporarily non-zero through fluctuations. It will be shown in section 3 that the deviations from a Lorentzian line shape observed in

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depolarized Rayleigh line broadening experiments for molecules with high rotational states are related to the results of the viscomagnetic effect and flow birefringence.

From the systematic comparison of data on the three effects information is obtained about the scalar factor of the polarization produced in viscous flow. As discussed in section 4 the range of possible expressions is narrowed down considerably. One of the simple expressions for the scalar factor which has been proposed in the literature is shown to agree with all results obtained so far for gases of "classical" linear molecules, although this solution is not unique.

2. The viscomagnetic effect and flow birefringence

2.1. Theory

The non-equilibrium state of a dilute gas is described by the distribution function $f = f^{(0)}(1 + \phi)$, with $f^{(0)}$ the Maxwell-Boltzmann distribution. In the case of viscous flow the formal solution of the linearized Waldmann-Snider equation reads (in the absence of external fields)

$$\phi = -\frac{\sqrt{2}}{n} \mathcal{R}^{-1} \phi^{20} : \overline{\mathbf{v}\mathbf{v}}. \quad (1)$$

Here \mathcal{R}^{-1} is the inverse of the linearized Waldmann-Snider collision operator and $\phi^{20} = \sqrt{2} \overline{\mathbf{W}\mathbf{W}}$ (for details of the notation see e.g. ref. 2). The operator \mathcal{R} is defined in a Maxwell-weighted Hilbert space of tensors built from the reduced peculiar velocity \mathbf{W} and the dimensionless angular momentum operator \mathbf{J} . The operator \mathcal{R}^{-1} is only defined outside the hydrodynamic subspace. A scalar product is defined according to

$$\langle A | B \rangle = \frac{1}{n} \text{Tr} \int_{-\infty}^{+\infty} A f^{(0)} B d^3c \quad (2)$$

(if A is self-adjoint; see ref. 2). A non-equilibrium average of a quantity which vanishes in equilibrium can thus be written as

$$\langle A \rangle = \langle A | \phi \rangle. \quad (3)$$

In order to represent \mathcal{R} a complete set of orthonormal expansion tensors is

defined

$$\phi^{pq_s} = \left\{ \left(\frac{2^p}{p!} \right) \frac{2q+1}{\langle [\mathbf{J}]^q \odot [\mathbf{J}]^q \rangle_0} \right\}^{1/2} [\mathbf{W}]^{(p)} [\mathbf{J}]^{(q)} P_s^{pq}. \tag{4}$$

Here \odot denotes a q -fold contraction over tensor indices. To each tensor of rank p in \mathbf{W} and q in \mathbf{J} belongs a complete set of scalar factors P_s^{pq} which depend on W^2 and J^2 . If the factor $P_s^{pq} = 1$ the label s in ϕ^{pq_s} may be dropped (cf. the tensor ϕ^{20} in eq. (1)).

The transport properties of a gas can all be expressed in terms of matrix elements of the operator \mathcal{R}^{-1} with respect to the basis functions ϕ^{pq_s} . The viscosity tensor, for example, is found from the non-equilibrium average of the momentum flux ϕ^{20} , which is proportional to the stress tensor

$$\overline{\Pi} = -2kT \langle \phi^{20} | \mathcal{R}^{-1} \phi^{20} \rangle; \quad \overline{\nabla v} = -2\eta : \overline{\nabla v}. \tag{5}$$

Since \mathcal{R} is a scalar operator, the inverse matrix element $\langle \phi^{20} | \mathcal{R}^{-1} \phi^{20} \rangle$ can be written as a product of a trivial isotropic tensor and a reduced scalar matrix element given by

$$S^{-1}(20) \equiv \frac{1}{5} \langle \phi^{20} : \mathcal{R}^{-1} \phi^{20} \rangle_0. \tag{6}$$

Truncation of the basis set allows straightforward matrix inversion, so that in lowest approximation the shear viscosity is given by

$$\eta = \frac{kT}{S(20)}. \tag{7}$$

The scalar matrix elements are proportional to effective collision cross sections

$$S_{(p'q's')}^{(pq_s)} \equiv \langle v \rangle_0 \mathfrak{S}_{(p'q's')}^{(pq_s)}, \tag{8}$$

so that in first approximation

$$\eta = \frac{kT}{\langle v \rangle_0 \mathfrak{S}(20)}. \tag{9}$$

In a second approximation coupling to tensors anisotropic in \mathbf{J} has to be taken into account. This coupling is a consequence of the non-spherical interaction. The presence of these "polarizations" leads in general to field effects on the transport properties and to optical effects such as flow bire-

fringence. In this section we will concentrate on viscous flow of gases of linear molecules in a $^1\Sigma$ electronic ground state.

Experiments on the viscomagnetic effect (VME) have clearly established that for such gases the predominant polarization in viscous flow is of second rank in \mathbf{J} . Moreover, the data are very well described by a single moment curve (see refs. 3–7).

A single moment description only results if the following assumptions are true:

– A single tensor $\phi^{02\pi}$ (out of the set ϕ^{02s}) couples to the momentum flux ϕ^{2i} (through \mathcal{R}_{nd} , see e.g. ref. 8):

$$\frac{1}{5}\langle\phi^{02s} : \mathcal{R}\phi^{20}\rangle = \delta_{s\pi}\langle v \rangle_0 \mathfrak{E}(02\pi). \quad (10)$$

This tensor is given by

$$\phi^{02\pi} = P_{\pi}^{02} \left(\frac{15}{2}\right)^{1/2} \frac{\overline{\mathbf{J}\mathbf{J}}}{\langle \mathbf{J}^2(\mathbf{J}^2 - \frac{3}{4}) \rangle_0^{1/2}}, \quad (11)$$

with a normalization condition for P_{π}^{02} reading

$$\langle (P_{\pi}^{02})^2 \mathbf{J}^2(\mathbf{J}^2 - \frac{3}{4}) \rangle_0 = \langle \mathbf{J}^2(\mathbf{J}^2 - \frac{3}{4}) \rangle_0. \quad (12)$$

– The tensor $\phi^{02\pi}$ is an eigenfunction of \mathcal{R} in the subspace of functions anisotropic in \mathbf{J} (or an eigenfunction of \mathcal{R}_d , see e.g. ref. 8), so that

$$\langle \phi^{02s} : \mathcal{R}\phi^{02\pi} \rangle_0 = 5\delta_{s\pi}\langle v \rangle_0 \mathfrak{E}(02\pi). \quad (13)$$

Note that the other tensors of the set ϕ^{02s} need not be eigenfunctions of \mathcal{R}_d . A consequence of eq. (13) is that

$$\langle \phi^{02\pi} : \mathcal{R}^{-1}\phi^{02\pi} \rangle_0 = 5\{\langle v \rangle_0 \mathfrak{E}(02\pi)\}^{-1}, \quad (14)$$

as the off-diagonal coupling to ϕ^{20} may be neglected (typically $\{\mathfrak{E}(02\pi)/\mathfrak{E}(02\pi)\} \approx 0.05$).

The parameters follow from a fit of the resulting single moment curve to the data of the viscomagnetic effect^{3–6}:

$$\psi_{02\pi} = \frac{\mathfrak{E}(02\pi)^2}{\mathfrak{E}(20)\mathfrak{E}(02\pi)}, \quad (15)$$

representing the magnitude of the effect, and

$$\left(\frac{B}{p}\right)_{\omega\tau=1} = \frac{\hbar}{|g|\mu_n kT} \langle v \rangle_0 \Xi(02\pi), \tag{16}$$

representing the position of the effect on the B/p axis for which the precession angle $\omega\tau$ is unity. The decay cross section $\Xi(02\pi)$ and the absolute value of the production cross section $\Xi_{(20)}^{(02\pi)}$ can therefore be obtained from these experiments. Consequently, it is also possible to determine the inverse matrix element

$$S^{-1}_{(20)}^{(02\pi)} \equiv \frac{1}{\xi} \langle \phi^{02\pi} : \mathcal{R}^{-1} \phi^{20} \rangle_0 = - \frac{\Xi_{(20)}^{(02\pi)}}{\langle v \rangle_0 \Xi(20) \Xi(02\pi)}. \tag{17}$$

In flow birefringence (FBR) experiments the non-equilibrium average of the tensor

$$\phi^{0\dot{2}} = \left(\frac{15}{2}\right)^{1/2} \left\langle \frac{J^2}{J^2 - \frac{3}{4}} \right\rangle_0^{-1/2} \frac{\overline{JJ}}{J^2 - \frac{3}{4}} \tag{18}$$

is directly observed (see refs. 9 and 10). This average is proportional to the inverse matrix element

$$S^{-1}_{(20)}^{(0\dot{2})} \equiv \frac{1}{\xi} \langle \phi^{0\dot{2}} : \mathcal{R}^{-1} \phi^{20} \rangle_0, \tag{19}$$

which can therefore be determined from the FBR data (see refs. 10 and 11).

According to the assumptions made before (eqs. (10) and (13))

$$\langle \phi^{0\dot{2}} : \mathcal{R}^{-1} \phi^{20} \rangle_0 = \frac{1}{\xi} \langle \phi^{0\dot{2}} : \phi^{02\pi} \rangle_0 \langle \phi^{02\pi} : \mathcal{R}^{-1} \phi^{20} \rangle_0. \tag{20}$$

The overlap integral

$$a_\pi \equiv \frac{1}{\xi} \langle \phi^{0\dot{2}} : \phi^{02\pi} \rangle_0 = \frac{S^{-1}_{(20)}^{(0\dot{2})}}{S^{-1}_{(20)}^{(02\pi)}} \tag{21}$$

can thus be obtained from a comparison of VME and FBR. By substitution of eqs. (11) and (18) in eq. (21) it is seen that

$$a_\pi = \left\{ \left\langle \frac{J^2}{J^2 - \frac{3}{4}} \right\rangle_0 \langle J^2 (J^2 - \frac{3}{4}) \rangle_0 \right\}^{-1/2} \langle J^2 P_\pi^{02} \rangle_0. \tag{22}$$

A determination of the overlap integral a_π can therefore yield interesting information about the scalar factor of the polarization produced in viscous flow.

If only a single rotational level is excited, this expression reduces to

$$a_{\pi} = \langle P_{\pi}^{02} \rangle_0 \quad \text{“single level case”} . \quad (23)$$

Clearly P_{π}^{02} does not depend on J^2 in such a case, but it can still depend on W^2 . However, if P_{π}^{02} does not depend on W^2 a_{π} must be equal to unity in a single level case.

If, on the other hand, mainly high rotational states are excited (“classical” linear molecules), eq. (22) may be approximated by

$$a_{\pi} = \langle J^4 \rangle_0^{-1/2} \langle J^2 P_{\pi}^{02} \rangle_0 \quad \text{“classical linear molecules”} . \quad (24)$$

2.2. Results for classical linear molecules

In table I the room temperature data available for “classical” linear molecules are listed. These data have been obtained from the shear viscosity, the viscomagnetic effect and flow birefringence (see ref. 10). (For a review of the various experimental quantities see ref. 12.) Also listed are the values for $|a_{\pi}|$ calculated from these data according to eq. (21). Within the experimental uncertainties $|a_{\pi}| = 0.70 \approx (2)^{-1/2}$ for these molecules.

In order to study the temperature dependence of a_{π} , FBR measurements have been performed over a temperature range from 90 to 293 K for N_2 and CO (see ref. 11). VME data are already available for these gases. The results for $|S^{-1}(02\pi)|$ from the VME and for $S^{-1}(02\pi)$ from FBR have been plotted in figs. 1 and 2 together with the values obtained for a_{π} . It is shown that for N_2 and CO $|a_{\pi}|$ remains at a constant value $0.70 \approx 2^{-1/2}$ in the temperature range investigated.

The normalization of ϕ^{02} and $\phi^{02\pi}$ requires that $|a_{\pi}| \leq 1$. The results for $|a_{\pi}|$ fulfill this requirement. Since the value for $|a_{\pi}|$ is neither 0 nor 1, the tensor ϕ^{02} does not belong to the basis set ϕ^{02s} .

TABLE I
Results derived from the viscomagnetic effect^{4,6} and from flow birefringence¹⁰ for classical linear molecules at 293 K. The estimated uncertainties for a_{π} are 7%.

Gas	m_r	θ (K)	$\mathfrak{S}(20)$ (10^{-20} m^2)	$\mathfrak{S}(02\pi)$ (10^{-20} m^2)	$ \mathfrak{S}(\frac{02\pi}{20}) $ (10^{-20} m^2)	$ S^{-1}(\frac{02\pi}{20}) $ (10^{14} s m^{-3})	$-S^{-1}(\frac{02\pi}{20})$ (10^{14} s m^{-3})	$ a_{\pi} $
N_2	28.00	2.88	34.6	23.7	1.50	2.74	1.97	0.72
CO	28.01	2.78	34.7	23.5	2.02	2.69	1.97	0.73
N_2O	44.01	0.60	52.4	64	3.52	1.98	1.34	0.68
CO_2	44.01	0.56	52.2	68	3.86	2.05	1.38	0.67
OCS	60.07	0.29	73.5	79	4.76	1.80	1.19	0.66

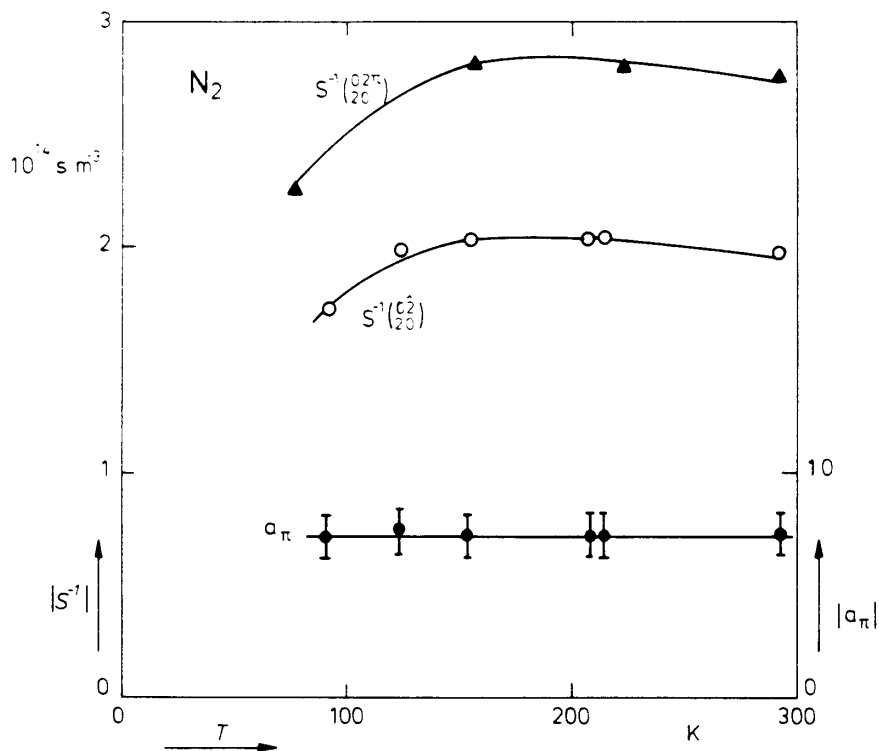


Fig. 1. Results derived from viscomagnetic effect and from flow birefringence for N_2 . Estimated error 5% for $S^{-1}(22^\pi)$ and $S^{-1}(20^\pi)$, and 7% for a_π .

In section 4 the implications of these results for the possible expressions for the scalar factor P_π^{02} will be discussed.

2.3. Results for hydrogen isotopes

In table II the results derived from VME and FBR data are listed for the various modifications of the hydrogen isotopes at 293 K, while in figs. 3 and 4 the available data from the VME and from the study of the temperature dependence of FBR (see ref. 11) are plotted for oD_2 and HD. Again $|a_\pi| \leq 1$ as required.

For pH_2 at 293 K and oD_2 at $T < 200$ K the "single level case" (see subsection 2.1) is approximately reached. It is found that for these gases $|a_\pi| = 1$ within the experimental uncertainties (see table II and fig. 3). This confirms the assumption that P_π^{02} does not depend on the translational energy W^2 .

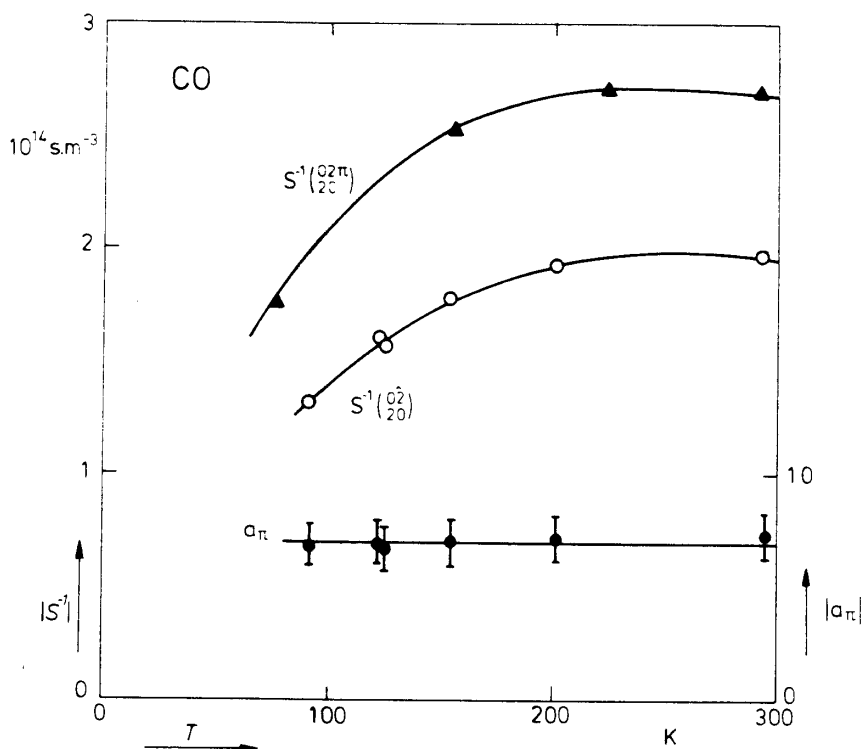


Fig. 2. Results derived from the viscomagnetic effect and from flow birefringence for CO. Estimated error 5% for $S^{-1}(\frac{02\pi}{20})$ and $S^{-1}(\frac{02}{20})$, and 7% for a_{π} .

For HD $|a_{\pi}|$ varies from 0.90 at 90 K to 0.83 at 293 K, illustrating the transition from the single level case to the "classical" case.

For $n\text{H}_2$ and $n\text{D}_2$ at 293 K (see table II) no simple conclusions can be drawn, since these gases have to be treated as mixtures of ortho and para species.

TABLE II

Results derived from the viscomagnetic effect^{5,6}) and from flow birefringence¹⁰) for modifications of the hydrogen isotopes at 293 K. The experimental uncertainties in a_{π} are estimated 12% (except for HD: 7%).

Gas	m_r	θ (K)	$\mathfrak{E}(20)$ (10^{-20} m^2)	$\mathfrak{E}(02\pi)$ (10^{-20} m^2)	$ \mathfrak{E}(\frac{02\pi}{20}) $ (10^{-20} m^2)	$ S^{-1}(\frac{02\pi}{20}) $ (10^{14} s m^{-3})	$-S^{-1}(\frac{02}{20})$ (10^{14} s m^{-3})	$ a_{\pi} $
oH_2	2.016	85.3	18.4				0.21	
pH_2	2.016	85.3	18.4	0.49	0.019	0.846	0.78	0.92
nH_2	2.016	85.3	18.4	0.51	0.0133	0.569	0.31	0.54
HD	3.021	64.3	18.7	2.26	0.282	3.28	2.72	0.83
oD_2	4.028	43.0	18.6	0.91	0.026	0.872	0.85	0.97
nD_2	4.028	43.0	18.6	0.88	0.027	0.937	0.76	0.81

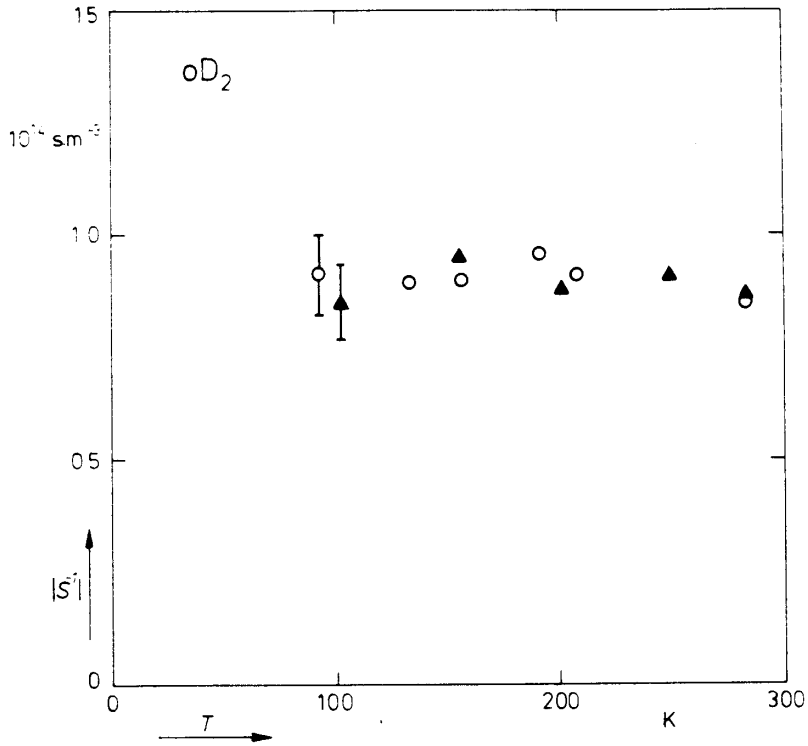


Fig. 3. Results derived from the viscomagnetic effect (▲) and from flow birefringence (○) for oD_2 . Typical error bars are indicated. The overlap integral $|a_{\nu}| = S^{-1}(\frac{1}{2}\phi_{\nu}^2)/S^{-1}(\frac{1}{2}\phi_{\nu}^{2\pi}) \approx 1$ (not drawn).

3. The broadening of the depolarized Rayleigh line

3.1. Theory

In section 2 a complete set of functions ϕ^{02s} of second rank in \mathbf{J} has been introduced. One of these tensors, $\phi^{02\pi}$, is relevant for a single moment description of the viscomagnetic effect; $\phi^{02\pi}$ has therefore been assumed to be an eigenfunction of \mathcal{R} in the subspace spanned by the set ϕ^{02s} . The other elements of this set need not be eigenfunctions. In agreement with the results of section 2 it will here be assumed that the scalar factors P_s^{02} depend on \mathbf{J}^2 only.

Orientational fluctuations are at the origin of the collisional broadening of the depolarized Rayleigh line (DPR)¹³⁻¹⁶, see also ref. 17. The Fourier transform of the line shape is the time correlation function of the tensor ϕ^{02} .

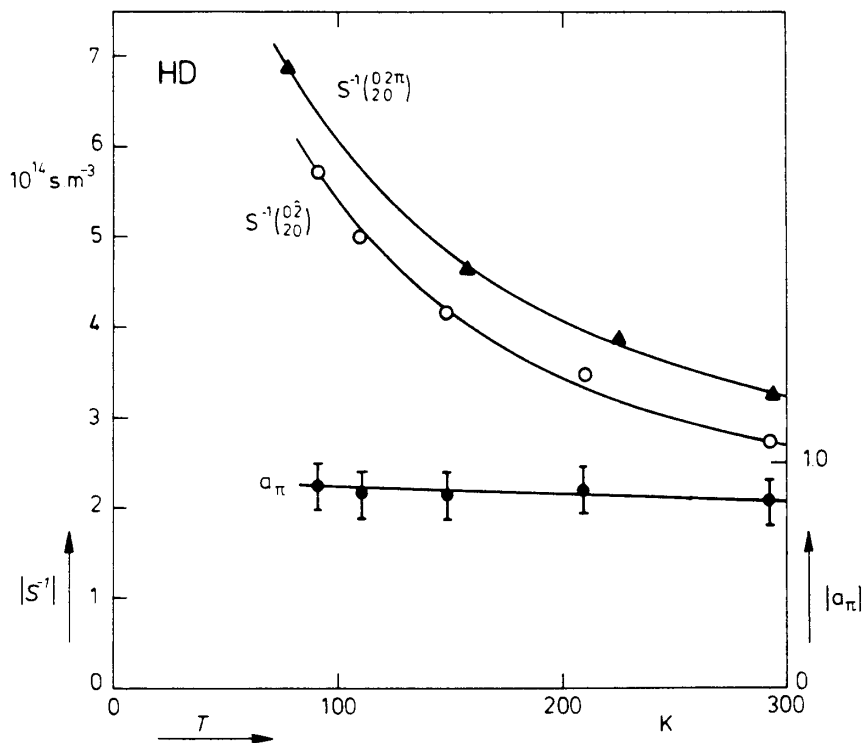


Fig. 4. Results derived from the viscomagnetic effect and from flow birefringence for HD. Estimated error 5% for $S^{-1}(\frac{02^0}{20})$ and $S^{-1}(\frac{02^\pi}{20})$, and 7% for a_π .

which is also relevant in the description of flow birefringence (see eq. (18)):

$$C(t) \equiv \frac{1}{5} \langle \phi^{02}(0) : \phi^{02}(t) \rangle_0. \quad (25)$$

The time evolution of ϕ^{02} can be written as

$$\phi^{02}(t) = e^{-n\mathcal{R}t} \phi^{02}(0), \quad (26)$$

with \mathcal{R} the linearized Waldmann–Snider collision operator and n the number density. Consequently,

$$C(t) = \frac{1}{5} \langle \phi^{02} : e^{-n\mathcal{R}t} \phi^{02} \rangle_0. \quad (27)$$

According to section 2 the overlap integral a_π of ϕ^{02} and $\phi^{02\pi}$ has a value between 0.5 and 1 for all linear molecules studied. The tensor ϕ^{02} therefore does not belong to the set ϕ^{02s} . An exception is formed by the trivial case of

single level systems (such as pH_2 and HD at sufficiently low temperatures) for which the set ϕ^{02s} collapses into a single element ϕ^{02} (since there is no W^2 dependence).

It is always possible to express ϕ^{02} in terms of the set ϕ^{02s} according to

$$\phi^{02} = \sum_s a_s \phi^{02s} ; \quad \sum_s a_s^2 = 1 . \quad (28)$$

Apart from $\phi^{02\pi}$, which is an eigenfunction of \mathcal{R}_d , the elements of the set ϕ^{02s} may still be chosen freely. We will *define* one of its elements, $\phi^{02\rho}$, in such a way that

$$\phi^{02} = a_\pi \phi^{02\pi} + (1 - a_\pi^2)^{1/2} \phi^{02\rho} . \quad (29)$$

Three possible situations may now occur:

1) $\phi^{02\pi}$ and $\phi^{02\rho}$ are degenerate eigenfunctions of \mathcal{R}_d . Consequently ϕ^{02} will also be an eigenfunction of \mathcal{R}_d , and an exponential correlation function will result.

2) $\phi^{02\pi}$ and $\phi^{02\rho}$ are non-degenerate eigenfunctions of \mathcal{R}_d . Consequently ϕ^{02} is not an eigenfunction of \mathcal{R}_d . A two moment description of the correlation function will result (see below).

3) $\phi^{02\pi}$ is an eigenfunction of \mathcal{R}_d , but $\phi^{02\rho}$ is not. This would lead to a multimoment description of the correlation function.

In DPR experiments on "classical" linear molecules distinct deviations from an exponential time correlation function have been found¹⁸). Consequently $\phi^{02\pi}$ and $\phi^{02\rho}$ cannot be degenerate eigenfunctions of \mathcal{R} . It is now a logical step to try to construct a two moment description of the decay of ϕ^{02} (i.e. $\phi^{02\pi}$ and $\phi^{02\rho}$ are non-degenerate eigenfunctions of \mathcal{R}_d). This will henceforth be assumed. Essentially this assumption implies that ϕ^{02} couples only to tensors in the plane defined by $\phi^{02\pi}$ and ϕ^{02} itself. The space of tensors to which ϕ^{02} can couple is thus effectively two dimensional. It is spanned by the orthonormal eigenfunctions $\phi^{02\pi}$ and $\phi^{02\rho}$ or, equivalently, by the orthonormal pair of tensors ϕ^{02} and

$$\phi^{02D} = (1 - a_\pi^2)^{1/2} \phi^{02\pi} - a_\pi \phi^{02\rho} \quad (30)$$

(or opposite sign). A geometrical illustration of this situation is shown in fig. 5.

From a numerical analysis of the DPR line shape three parameters can be determined (see the appendix): the initial slope of the correlation function, the second derivative at $t = 0$, and the time integral $\int_0^\infty C(t) dt$. These quantities can now be related to effective cross sections. By expansion of the exponential in

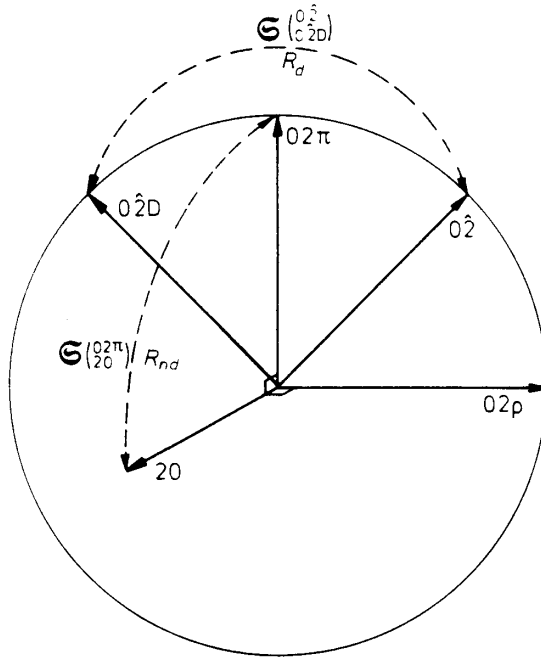


Fig. 5. Geometrical illustration of the second rank in J tensors relevant for a description of VME. FBR and DPR for the case $a_r = 1/\sqrt{2}$. The tensors $\phi^{02\pi}$ and $\phi^{02\rho}$ are assumed to be non-degenerate eigenfunctions of \mathcal{R} in the subspace of functions anisotropic in J .

eq. (27) the correlation function can be written as

$$C(t) = 1 - \frac{n}{5} \langle \phi^{02} : \mathcal{R} \phi^{02} \rangle_0 t + \frac{n^2}{10} \langle \phi^{02} : \mathcal{R} \mathcal{R} \phi^{02} \rangle_0 t^2 + \dots \tag{31}$$

In our two-dimensional space this becomes

$$C(t) = 1 - n \langle v \rangle_0 \mathfrak{S}(0\hat{2}) t + \frac{n^2}{2} \langle v \rangle_0^2 \{ \mathfrak{S}(0\hat{2})^2 + \mathfrak{S}(0\hat{2}D)^2 \} t^2. \tag{32}$$

The first time derivative of $C(t)$ is therefore given by

$$\left. \frac{dC(t)}{dt} \right|_{t=0} = -n \langle v \rangle_0 \mathfrak{S}(0\hat{2}). \tag{33}$$

For the second derivative we get

$$\left. \frac{d^2C(t)}{dt^2} \right|_{t=0} = n^2 \langle v \rangle_0^2 \{ \mathfrak{S}(0\hat{2})^2 + \mathfrak{S}(0\hat{2}D)^2 \}. \tag{34}$$

Finally the integral of the extrapolated correlation function yields the inverse matrix element $S^{-1}(0\hat{2})$:

$$\int_0^{\infty} C(t) dt = \frac{1}{n} S^{-1}(0\hat{2}). \quad (35)$$

It is easily verified that the reduced scalar cross section matrix of \mathcal{R} with respect to the basis $(\phi^{0\hat{2}}, \phi^{0\hat{2}D})$ can be written in terms of $\mathfrak{S}(02\pi)$ and $\mathfrak{S}(02\rho)$ according to

$$\begin{pmatrix} \mathfrak{S}(0\hat{2}) & \mathfrak{S}(0\hat{2}D) \\ \mathfrak{S}(0\hat{2}D) & \mathfrak{S}(0\hat{2}D) \end{pmatrix} = \begin{pmatrix} a_{\pi}^2 \mathfrak{S}(02\pi) + (1 - a_{\pi}^2) \mathfrak{S}(02\rho) & a_{\pi} (1 - a_{\pi}^2)^{1/2} \{ \mathfrak{S}(02\pi) - \mathfrak{S}(02\rho) \} \\ a_{\pi} (1 - a_{\pi}^2)^{1/2} \{ \mathfrak{S}(02\pi) - \mathfrak{S}(02\rho) \} & (1 - a_{\pi}^2) \mathfrak{S}(02\pi) + a_{\pi}^2 \mathfrak{S}(02\rho) \end{pmatrix}. \quad (36)$$

Straightforward matrix inversion thus yields an expression for $S^{-1}(0\hat{2})$ in terms of $\mathfrak{S}(02\pi)$ and $\mathfrak{S}(02\rho)$. It will be convenient, however, to express $S^{-1}(0\hat{2})$ and $\mathfrak{S}(0\hat{2}D)$ in terms of $\mathfrak{S}(0\hat{2})$ and $\mathfrak{S}(02\pi)$. For "classical" linear molecules it has been found from FBR and VME (see section 2) that $|a_{\pi}| = 2^{-1/2}$. In this case $\mathfrak{S}(0\hat{2}) = \mathfrak{S}(0\hat{2}D)$ (see eq. (36)), so that the resulting expressions are:

$$S^{-1}(0\hat{2}) = \frac{1}{\langle v \rangle_0} \frac{\mathfrak{S}(0\hat{2})}{2\mathfrak{S}(0\hat{2})\mathfrak{S}(02\pi) - \mathfrak{S}(02\pi)^2}, \quad (37)$$

and

$$|\mathfrak{S}(0\hat{2}D)| = \mathfrak{S}(02\pi) - \mathfrak{S}(0\hat{2}). \quad (38)$$

For simplicity these expressions will be used instead of those for arbitrary a_{π} , since the resulting error is small compared to the experimental uncertainties.

Since $\mathfrak{S}(02\pi)$ is known from the VME and $\mathfrak{S}(0\hat{2})$ from the initial slope of the DPR correlation function (see eq. (33)), it is now possible to calculate $|\mathfrak{S}(0\hat{2}D)|$ and $S^{-1}(0\hat{2})$ from eqs. (37) and (38), and to compare with the corresponding data derived from the curvature and time integral of the DPR correlation function (see eqs. (34) and (35)).

3.2. Results for classical linear molecules

Measurements of the depolarized Rayleigh line broadening at 293 K for

several linear molecules have been performed by Keijser et al.¹⁸); the data have been reanalyzed (see the appendix). Values for the cross sections $\mathfrak{S}(0\hat{2})$ and $|\mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}}|$ and the inverse matrix element $S^{-1}(0\hat{2})$ are calculated from these measurements according to eqs. (33) to (35). The results are listed in table III.

Also listed are the values for $|\mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}}|$ and $S^{-1}(0\hat{2})$ calculated from the experimental results for $\mathfrak{S}(0\hat{2})$ and $\mathfrak{S}(02\pi)$ according to eqs. (37) and (38). The agreement obtained between the two sets of data is very good. In the case of $|\mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}}|$ the agreement is even better than one might hope in view of the rather large experimental uncertainties (estimated 25%). The values for $S^{-1}(0\hat{2})$ are more accurately known (3%), but here it should be noted that this quantity is mainly determined by $\mathfrak{S}(0\hat{2})$, obtained from the initial slope of the correlation function.

Essentially the following conclusion has been obtained: a two moment description of the DPR line leads to results that are consistent with the single moment description of VME and FBR.

TABLE III

The cross section $\mathfrak{S}(02\pi)$ from the viscomagnetic effect (VME) and results for $\mathfrak{S}(0\hat{2})$, $|\mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}}|$ and $S^{-1}(0\hat{2})$ from depolarized Rayleigh line broadening (DPR) data listed in table IV in the appendix. Also tabulated are $|\mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}}|$ and $S^{-1}(0\hat{2})$ calculated from $\mathfrak{S}(02\pi)$ and from $\mathfrak{S}(0\hat{2})$ according to eqs. (37) and (38) (using the fact that $|a_{\pi}| \approx 2^{-1/2}$). For estimated uncertainties see text.

Gas	$\mathfrak{S}(02\pi)$	$\mathfrak{S}(0\hat{2})$	$ \mathfrak{S}_{(0\hat{2}D)}^{0\hat{2}} $		$S^{-1}(0\hat{2})$	
	(10^{-20} m^2)	(10^{-20} m^2)	(10^{-20} m^2)		(10^{14} s m^{-3})	
	VME	DPR	DPR	eq. (38)	DPR	eq. (37)
N ₂	23.7	35.5	10	11.8	47.0	47.6
CO	32.5	42.8	11	10.3	36.9	37.3
N ₂ O	64					
CO ₂	68	90.2	23	22	22.0	22.2
OCS	79	110	23	31	20.2	21.7

3.3. Results for hydrogen isotopes

For the hydrogen isotopes a multilevel treatment is in general necessary. We will refrain, therefore, from analyzing the small departure from a Lorentzian line shape observed for HD, nH₂ and nD₂ at 293 K¹⁹).

The gases HD and pH₂, however, have been studied at temperatures low enough for the single level limit to be reached (for pH₂ this is already the case around 293 K, while for HD the temperature has to be lower than 75 K). As shown in figs. 6 and 7, for these gases $\mathfrak{S}(0\hat{2})$ and $\mathfrak{S}(02\pi)$ are equal within the experimental uncertainties at sufficiently low temperatures. This is expected if

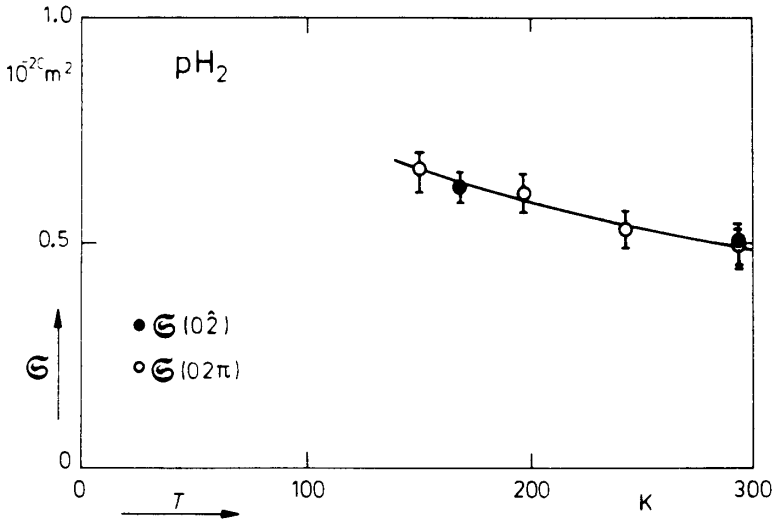


Fig. 6. The decay cross section $\bar{G}(02^1)$ derived from depolarized Rayleigh line broadening experiments and $\bar{G}(02^\pi)$ from the viscomagnetic effect for pH_2 as a function of temperature.

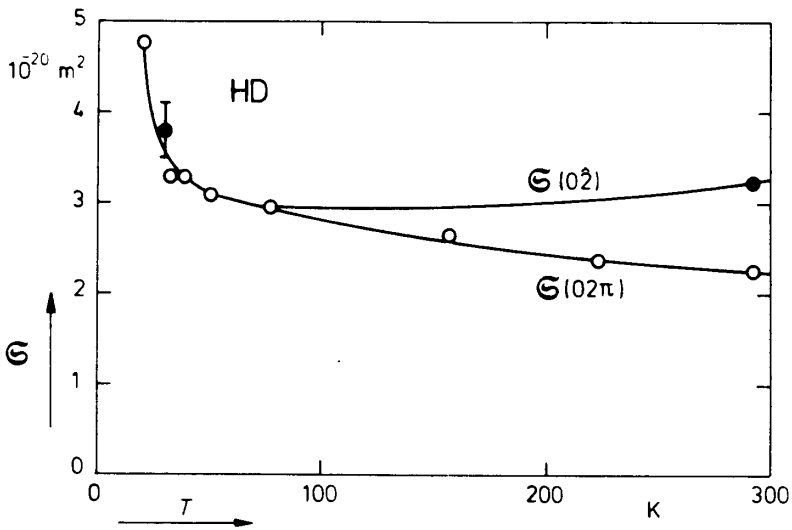


Fig. 7. The decay cross section $\bar{G}(02^1)$ derived from depolarized Rayleigh line broadening experiments and $\bar{G}(02^\pi)$ from the viscomagnetic effect for HD as a function of temperature.

P_{π}^{02} does not depend on W^2 (since then $\phi^{0\dot{2}} = \phi^{02\pi}$). This result thus confirms the conclusions of subsection 2.3.

4. Possible expressions for the scalar factor of the angular momentum polarization in viscous flow

In this section, dealing with "classical" linear molecules, the various expressions will all be given in a high j approximation. This will simplify the discussion, while the error made is quite small. The tensor $\phi^{02\pi}$ is thus given by

$$\phi^{02\pi} = \left(\frac{15}{2}\right)^{1/2} \frac{\overline{JJ}}{\langle J^4 \rangle_0^{1/2}} P_{\pi}^{02}. \quad (39)$$

with a normalization condition for P_{π}^{02} :

$$\langle (P_{\pi}^{02})^2 J^4 \rangle_0 = \langle J^4 \rangle_0. \quad (40)$$

The information obtained about P_{π}^{02} in sections 2 and 3 can be summarized as:

- 1) P_{π}^{02} does not depend on W^2 .
- 2) The overlap integral a_{π} between $\phi^{0\dot{2}}$ and $\phi^{02\pi}$ (see eq. (21)), which is related to P_{π}^{02} according to

$$a_{\pi} = \langle P_{\pi}^{02} J^2 \rangle_0 \langle J^4 \rangle_0^{-1/2}, \quad (41)$$

is a constant with an absolute value approximately equal to $2^{-1/2}$ (note that the same conclusions necessarily apply to the scalar factor P_{ρ}^{02} of the tensor $\phi^{02\rho}$ defined in section 3).

In the literature the discussion has so far been limited to two simple expressions for P_{π}^{02} :

$$P_{\pi}^{02} = 1; \quad \phi^{02\pi} = \left(\frac{15}{2}\right)^{1/2} \frac{\overline{JJ}}{\langle J^4 \rangle_0^{1/2}}, \quad (42)$$

and

$$P_{\pi}^{02} = \frac{\langle J^4 \rangle_0^{1/2}}{J^2}; \quad \phi^{02\pi} (= \phi^{0\dot{2}}) = \left(\frac{15}{2}\right)^{1/2} \frac{\overline{JJ}}{J^2}. \quad (43)$$

The first expression leads to $a_{\pi} = \langle J^2 \rangle_0 / \langle J^4 \rangle_0^{1/2} \approx 2^{-1/2}$ in the high j limit, while the second implies that $a_{\pi} = 1$.

It would therefore be tempting to conclude that the scalar factor P_{π}^{02} is equal to 1. It has now become clear, however, that this possible solution is by no means unique. This may be illustrated by the following example. In the discussion of DPR in section 3 the tensor $\phi^{02\rho}$ has been introduced. If $P_{\pi}^{02} = 1$, $\phi^{02\rho}$ would be given by (see eq. (29) with $a_{\pi} = 2^{-1/2}$)

$$\phi^{02\rho} = \left(\frac{15}{2}\right)^{1/2} \frac{\overline{JJ}}{J^2} \left\{ \sqrt{2} - \frac{J^2}{\langle J^4 \rangle_0^{1/2}} \right\}. \quad (44)$$

Also *this* tensor has an overlap of $2^{-1/2}$ with ϕ^{02} (see also fig. 5).

For a final conclusion as to the correct expression for P_{π}^{02} model calculations of the relevant cross sections will be needed. It will be useful to compare these cross sections with the results obtained here.

Appendix

Analysis of depolarized Rayleigh line broadening

Measurements of depolarized Rayleigh line broadening have been performed by Keijser et al.¹⁸). These measurements have been reanalyzed in order to obtain quantitative results for the second derivative of the second time derivative of the correlation function $C(t)$. Curve fit procedures were used to determine the first and second derivatives of $C(t)$ at $t = 0$, while a discrete Simpson approximation was used to evaluate the integral $\int_0^{\infty} C(t) dt$. The results are given in table IV. The notation of the various quantities is consistent with

TABLE IV
Results from the broadening of the depolarized Rayleigh line from ref. 18 (reanalyzed, see the appendix). Estimated error is 3% in Γ/n and $\tilde{\Gamma}/n$ and 50% in Γ_2/n^2 (n is the number density).

Gas	$2\pi \frac{\Gamma}{n}$ ($10^{-16} \text{ m}^3 \text{ s}^{-1}$)	$2\pi \frac{\tilde{\Gamma}}{n}$ ($10^{-16} \text{ m}^3 \text{ s}^{-1}$)	$4\pi^2 \frac{\Gamma_2}{n^2}$ ($10^{-32} \text{ m}^6 \text{ s}^{-2}$)
N ₂	2.36	2.13	0.46
CO	2.85	2.71	0.53
CO ₂	4.79	4.54	1.5
OCS	5.01	4.96	1.1

ref. 18:

$$2\pi\Gamma = - \left(\frac{dC(t)}{dt} \right)_{t=0}, \quad (\text{A.1})$$

$$2\pi\tilde{\Gamma} = \left[\int_0^{\infty} C(t) dt \right]^{-1}, \quad (\text{A.2})$$

$$4\pi^2\Gamma_2 = \left(\frac{d^2C(t)}{dt^2} \right)_{t=0} - \left[\left(\frac{dC(t)}{dt} \right)_{t=0} \right]^2. \quad (\text{A.3})$$

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