where $\square \overset{(l)}{\ldots_\lambda\ldots}$ is an isotropic tensor of rank $2l+1$ defined by [42]

$$\square^{(l)}_{\mu_1..\mu_l,\lambda,\mu_1'.,\mu_l'} = \Delta^{(l)}_{\mu_1..\mu_l.\nu_1..\nu_{l-1}\nu_l} \; \varepsilon_{\nu_l\lambda\nu_l} \; \Delta^{(l)}_{\nu_l'\nu_1.\nu_{l-1},\mu_1'..\mu_l'}$$

$$= \frac{l+1}{l} \frac{2l+3}{2l+1} \Delta^{(l+1)}_{\mu_1..\mu_l\mu,\mu'\mu_1'..\mu_l'} \varepsilon_{\mu\mu'\lambda}. \quad \text{(II.13)}$$

The normalization of this tensor is given by:

$$\varepsilon_{\mu_l\lambda\mu_l'} \square^{(l)}_{\mu_1..\mu_{l-1}\mu_l,\lambda,\mu_1..\mu_{l-1}\mu_l'} = \frac{l+1}{l} (2l+1). \quad \text{(II.14)}$$

Thus, due to (II.11 and II.12) one has the following commutation relations for the Cartesian operators:

$$[J_\lambda, T^{jj'}_{\mu_1..\mu_l}] = -il \, \square^{(l)}_{\mu_1,.\mu_l,\lambda,\nu_1..\nu_l} \, T^{jj'}_{\nu_1,.\nu_l}. \quad \text{(II.15)}$$

For $j' = j$ the lth rank tensor operator is proportional to the lth rank irreducible tensor constructed from the Cartesian components of $\boldsymbol{J}$ (cf. Ref. [19]):

$$\sqrt{2j+1}\, T^{jj'}_{\mu_1,.\mu_l} = \sqrt{(2l+1)\,!!/l!}$$

$$\cdot P_j (J_0 J_1 \ldots J_{l-1})^{-1} \overline{J_{\mu_1} \ldots J_{\mu_l}}, \quad \text{(II.16)}$$

where

$$P_j = \sum_M |jM\rangle\langle jM|, \quad P_j J^2 = j(j+1) P_j, \text{ and}$$

$$J_k^2 = J^2 - \tfrac{1}{2} k(\tfrac{1}{2}k+1). \quad \text{(II.17)}$$

On the Pressure Dependence of the Transport Properties of Dilute Polyatomic Gases

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It is shown that the transport coefficients of dilute polyatomic gases in the ordinary Navier-Stokes regime contain an extra pressure dependence when the internal state Hamiltonian does not commute with the nonequilibrium distribution function-density matrix for the gas. As a specific example, the pressure dependence of the shear viscosity of a gas of paramagnetic $^2\Sigma$ molecules is considered. Furthermore, the pressure dependence of the Senftleben and Senftleben-Beenakker effects is discussed and examples are given of the different types of molecules for which pressure dependence in the field-free as well as in the field-dependent transport coefficients may be expected.

The transport properties of polyatomic gases can be calculated from the linearized Waldmann-Snider equation

$$(\boldsymbol{p}/m) \cdot \nabla \ln f^{(0)} = \mathbb{J}_0 \, \varphi - (i/\hbar) \, [\mathcal{H}^{(\text{int})}, \varphi]_-\,, \quad (1)$$

where $f^{(0)}$ is the local equilibrium distribution function-density matrix given by

$$f^{(0)} = n\, Q^{-1} (2\pi m k T)^{-3/2} \exp\{-W^2 - \mathcal{H}^{(\text{int})}/kT\}$$

with Q the internal state partition function and $\boldsymbol{W}$ the reduced peculiar velocity $\boldsymbol{W} = (m/2kT)^{1/2} \boldsymbol{V}$. Furthermore, $\mathbb{J}_0$ is the (dissipative) collision superoperator representing the effect of binary collisions

and defined by

$$\mathbb{J}_0 \, \varphi \equiv (2\pi)^4 \hbar^2 \, \text{tr}_1 \int \mathrm{d}\boldsymbol{p}_1 \, f_1^{(0)}$$
$$\cdot \{ \int t_{g'}^g (\varphi' + \varphi_1') \, \delta(E) \, t_{g'}^{g\dagger} \, \mathrm{d}\boldsymbol{p}'$$
$$- (i/2\pi) [t_g^g (\varphi + \varphi_1) - (\varphi + \varphi_1) \, t_g^{g\dagger}] \},$$

where the quantities $t_{g'}^g$ and $t_g^{g\dagger}$ represent the (binary collision) transition operator and its adjoint (these are matrix elements in linear momentum space but still operators in the internal state space), a prime denotes a functional dependence on $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$, the

linear momenta of the molecule and its colliding partner, respectively, before a collision rather than on p and p_1, and tr_1 denotes a trace over the internal states of the collision partner. The quantity φ is an operator describing the deviation of the total distribution function f from its local equilibrium value $f^{(0)}$. The operator $\mathcal{H}^{(int)}$ is the Hamiltonian for internal states which consists, in general, of a number of different terms amongst which can be found the ordinary rotational energy term, the spin-rotation coupling term present in all paramagnetic molecules, the pseudo-quadrupolar coupling terms for paramagnetic molecules having more than one unpaired electron, spin-orbit couplings for paramagnetic molecules having electrons with orbital angular momentum, centrifugal stretching contributions, hindered rotation and, for some molecules, inversion. Moreover, various nuclear hyperfine couplings can be present for molecules whose constituent atoms possess nuclear spin. In the presence of magnetic and electric fields, this operator also contains the familiar Zeeman and Stark terms. As is well known, these latter two terms are necessary in order to obtain results for the ordinary SENFT-LEBEN and SENFTLEBEN-BEENAKKER effects [1-4]. For paramagnetic gases, the spin-rotation, pseudo-quadrupolar and spin-orbit couplings have been shown to play a significant rôle in determining the form taken by the field effects [5-8]. Inversion and hindered rotation, being of the same order of magnitude as the spin-rotation coupling in paramagnetic molecules, can be expected to play a similar rôle in transport phenomena. In every case the centrifugal stretching and nuclear hyperfine coupling terms can be neglected as their influence will certainly be too small to be detected with methods currently available.

In kinetic theory, the distribution function for the gas is expanded in terms of the microscopic variables available. For noble gases, the only available vectorial quantity is W. All polyatomic gases however, possess two such quantities, W and N, the

(nuclear) rotational angular momentum of the molecule. Moreover, should the molecule be paramagnetic, additional angular momenta such as S, the electronic spin and L, the electronic orbital angular momenta must be taken into account while, should the molecules be polar, the electric dipole moment $\mu^{(e)}$ has also to be considered. For symmetric top molecules, for example, for which the largest part of $\mu^{(e)}$ is the diagonal part, this amounts to an expansion in [9] W, N and N_ζ, the projection of N along the molecular figure axis. Asymmetric top molecules, having three principal axes with moments of inertia and dipole moments in arbitrary ratios require the full $\mu^{(e)}$ in the expansion.

Section 1 of this paper is devoted to a short discussion of the manner in which a pressure dependence can arise in the transport coefficients. In section 2, an explicit expression is obtained for the field-free pressure dependence in a gas of paramagnetic $^2\Sigma$ molecules since this case is the simplest to treat. In this same section, a very crude estimate will also be given of the size of the pressure effects to be expected. The final section, § 3, gives a discussion of the pressure effects both in the presence of and in the absence of an external magnetic field. In particular, a physical picture is suggested which makes plausible certain explicit results which have been obtained for the pressure dependence of the Sentleben effect for $^2\Sigma$ molecules [6].

1. The Basis of the Pressure Dependence

With the exception of $\mathcal{H}_{rot}$, and for $^2\Pi$ molecules [8], of $\mathcal{H}_{so}$ (spin-orbit coupling), the various parts of $\mathcal{H}^{(int)}$ can normally be neglected in the local equilibrium distribution function since they are rather small when compared with the thermal energy kT. In the procedures followed in normal kinetic theory, the perturbation $f^{(0)} \varphi$ of f from $f^{(0)}$ is expanded in terms of the available molecular quantities present in the system. Generally speaking, not every term of the expansion will commute with

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[9] A. C. LEVI, F. R. McCOURT, and A. TIP, Physica 39, 165 [1968].

$\mathcal{H}^{(\text{int})}$. Now, examining the Waldmann-Snider equation, it can be seen that because of this non-commutation, the term $(i/\hbar)\,[\mathcal{H}^{(\text{int})},\varphi]_-$ will give rise to contributions proportional to n^{-1} in addition to the normal density-independent contributions arising through $\mathcal{I}_0$. A formal expression for the field-free shear viscosity will be utilized here as an example. The integral equation obtained from Eq. (1) for the shear viscosity (for which $\varphi = -\mathbf{B} : [\nabla \boldsymbol{v}_0]^{(2)}$) is

$$-2[\boldsymbol{W}]^{(2)} = \mathcal{I}_0\,\mathbf{B} - (i/\hbar)\,[\mathcal{H}^{(\text{int})}, \mathbf{B}]_- . \quad (2)$$

The second rank irreducible tensor $\mathbf{B}$ can be expanded formally as

$$\mathbf{B} = [\boldsymbol{W}]^{(2)} B^{20} + \tilde{\mathbf{b}}\,B'. \quad (3)$$

Here the symbols $\mathbf{b}$ and B' denote column vectors of expansion tensors and of expansion coefficients, respectively, while a tilde indicates a transpose, $\tilde{\mathbf{b}}$,

e. g., being a row vector whose elements are irreducible second rank tensors. Insertion of expansion (3) into Eq. (2) together with the formation of the appropriate moments with the expansion tensors yields a set of coupled algebraic equations given by:

$$-n^{-1} = \beta_0\,B^{20} + \tilde{\boldsymbol{\beta}}_1\,B',$$
$$0 = \boldsymbol{\beta}_1 B^{20} + \boldsymbol{\beta}_2\,B' - (i/5\,n\,\hbar)$$
$$\cdot \langle \mathbf{b} : [\mathcal{H}^{(\text{int})}, \tilde{\mathbf{b}}]_-\rangle_0\,B'. \quad (4)$$

Here

$$\beta_0 = (5\,n)^{-1}\,\langle\,[\boldsymbol{W}]^{(2)} : \mathcal{I}_0[\boldsymbol{W}]^{(2)}\rangle_0,$$
$$\boldsymbol{\beta}_1 = (5\,n)^{-1}\,\langle\,[\boldsymbol{W}]^{(2)} : \mathcal{I}_0\,\mathbf{b}\rangle_0$$

(a vector whose elements are purely non-diagonal collison integrals) and $\boldsymbol{\beta}_2 = (5\,n)^{-1}\langle\mathbf{b} : \mathcal{I}_0\,\tilde{\mathbf{b}}\rangle_0$ (a matrix whose elements are collision integrals). The solution of Eqs. (4) together with the relation $\eta_0 = \frac{1}{2} n\,k\,T\,B^{20}$ gives the field-free shear viscosity as

$$\eta_0 = \frac{-\frac{1}{2}\,kT}{\beta_0 - \tilde{\boldsymbol{\beta}}_1\boldsymbol{\beta}_2^{-1}\,[1 - (i/5\,n\,\hbar)\,\langle\mathbf{b} : [\mathcal{H}^{(\text{int})}, \tilde{\mathbf{b}}]_-\rangle_0\,\boldsymbol{\beta}_2^{-1}]^{-1}\,\boldsymbol{\beta}_1} . \quad (5)$$

Recall that the negative-definiteness of $\mathcal{I}_0$ means that β_0, e. g., is a negative quantity. The average $\langle\ \rangle_0$ employed here denotes that in which $n^{-1} f^{(0)}$ is used as the weight function. All density dependenc has been explicitly included in order to make this formula as transparent as possible. Equation (5) shows all general features to be expected for the density dependence discussed here. If $\mathcal{H}^{(\text{int})}$ commutes with $\mathbf{b}$, Eq. (5) reduces to an expression containing the pressure-independent contributions from all expansion tensors employed. This is also the case in the high pressure limit. A particular property of $\mathcal{H}^{(\text{int})}$ used in obtaining expression (5) is that it contains no externally applied anisotropies: this means of course that the effect of external electric and magnetic fields cannot be considered in so simple a manner.

The characteristic pressure regions in which density effects will be observed are directly determined by the magnitudes of those parts of $\mathcal{H}^{(\text{int})}$ which do not commute with certain of the expansion terms. The size of these effects is also related, in an indirect way, to $\mathcal{H}^{(\text{int})}$ insofar as $\mathcal{H}^{(\text{int})}$ determines which terms must appear to lowest order in the expansion. The magnitude is determined in fact both by the matrix which describes the collisional coupling amongst the angular-momentum-dependent expansion tensors [as contained in the matrix $\boldsymbol{\beta}_2$ in Eq. (5)] and by the vector which describes their

collisional coupling with those angular-momentum-independent expansion tensors which directly determine the actual transport coefficients themselves [as contained in the vector $\boldsymbol{\beta}_1$ in Eq. (5)].

Paramagnetic and polar molecules in some sense behave analogously but manifest their differences from diamagnetic nonpolar molecules in different ways. The effects in a paramagnetic gas can be traced to two sources: in the first place, the expansion considered must take the electronic spin and/or orbital angular momenta properly into account and in the second place, the presence of these electronic angular momenta in the molecule gives rise to a number of new terms in the internal state Hamiltonian which have the property that not every term in the expansion of the distribution function commutes with them. For polar diamagnetic molecules, the situation is slightly different. Although, again, the expansion must properly take into account the presence of an additional molecular quantity, here $\boldsymbol{\mu}^{(e)}$, there is no corresponding addition of new terms to $\mathcal{H}^{(\text{int})}$ but rather, that part of the expansion connected to $\boldsymbol{\mu}^{(e)}$ no longer commutes with $\mathcal{H}_{\text{rot}}$. In this sense, the behaviour of paramagnetic and of polar molecules can be said to be fundamentally different. Of course, the possibility of having both paramagnetic and polar character exists and is, in fact, rather common.

2. A Specific Example — A Gas of $^2\Sigma$ Molecules

As an example of the density dependence discussed in the previous section, the field-free shear viscosity for a gas of paramagnetic doublet molecules with no electronic orbital angular momentum will now be considered. The internal state Hamiltonian for such molecules is, in general, given by

$$\mathcal{H}^{(\text{int})} = \tfrac{1}{2}\hbar^2 \mathbf{I}^{-1} : \mathbf{N}\mathbf{N} + \hbar\, \mathbf{N}\cdot\mathbf{C}\cdot\mathbf{S}, \qquad (6)$$

where $\mathbf{I}$ is the moment of inertia tensor and $\mathbf{C}$ the spin-rotation coupling tensor. In the case for which both $\mathbf{I}$ and $\mathbf{C}$ are isotropic, i. e., for linear $^2\Sigma$ molecules, this Hamiltonian simplifies to

$$\mathcal{H}^{(\text{int})} = (\hbar^2/2\,I)\, N^2 + c\,\hbar\, \mathbf{N}\cdot\mathbf{S}. \qquad (7)$$

In calculating the shear viscosity for this specific example, it is useful to write down an explicit form for the expansion of $\mathbf{B}$. The expansion used here is [5]

$$\begin{aligned}
\mathbf{B} =\ & [\mathbf{W}]^{(2)} B^{200} + P^{(+)}[\mathbf{N}]^{(2)} P^{(+)} B^{021} \\
& + P^{(-)}[\mathbf{N}]^{(2)} P^{(-)} B^{022} + (P^{(+)}[\mathbf{N}]^{(2)} P^{(-)} \\
& + P^{(-)}[\mathbf{N}]^{(2)} P^{(+)}) B^{023} + i(P^{(+)}[\mathbf{N}]^{(2)} P^{(-)} \\
& - P^{(-)}[\mathbf{N}]^{(2)} P^{(+)}) B^{024}.
\end{aligned} \qquad (8)$$

The first two of the superscripts "ijk" on the B's denote the ranks of the irreducible tensors in $\mathbf{W}$ and in $\mathbf{N}$ contained in the expansion term while the third superscript indicates the specific combinations of the spin-dependent projection operators $P^{(+)}$ and $P^{(-)}$ which define projections onto the two spin states of the molecule. In the case now under consideration, the presence of the electronic spin angular momentum $\mathbf{S}$ has necessitated the form of the expansion (8) and has resulted in the addition of the spin-rotation coupling term to (7): it is clear that the commutator of $\mathbf{S}\cdot\mathbf{N}$ couples the expansion terms containing $P^{(+)}\dots P^{(-)}$ and $P^{(-)}\dots P^{(+)}$. If the collisional coupling amongst the four latter terms of expansion (8) is represented by the 4×4 matrix $\mathcal{R}_0$ of the semi-diagonal collision brackets [10], i. e., if $(\mathcal{R}_0)_{ij} \equiv [{}^{02i}_{02j}]$ while the coupling caused by $c\,\mathbf{S}\cdot\mathbf{N}$ is represented by the 4×4 matrix $\mathcal{R}_1$ with all elements, except $(\mathcal{R}_1)_{34} = -(\mathcal{R}_1)_{43} \equiv a$, equal to zero, then the (field-free) shear viscosity is found to be

given by

$$\eta_0 = -\tfrac{1}{2}n^2\,k\,T\,\left\{ [{}^{200}_{200}] - \tilde{S}\,\mathcal{R}^{-1}\,S \right\}^{-1} \qquad (9)$$

where S is the column vector with $S_i \equiv [{}^{200}_{02i}]$ ($i=1$, 2, 3, 4) while $\mathcal{R} = \mathcal{R}_0 + \mathcal{R}_1$. When the traces over the electronic spin states have been performed, the following approximate relations hold [5]: $[{}^{021}_{021}] = [{}^{022}_{022}]$, $[{}^{023}_{023}] = [{}^{024}_{024}]$, $[{}^{200}_{021}] = [{}^{200}_{022}]$ and $[{}^{200}_{024}] = 0$. These relations are based on an assumption that the electronic spin is itself unaffected by the collisional process, an assumption which can be justified by the weakness of intermolecular magnetic dipole-magnetic dipole interactions with respect to the normal nonspherical parts of the intermolecular interaction potential. If these results are utilized, Eq. (9) becomes explicitly:

$$\eta_0 = \frac{-\tfrac{1}{2}n^2\,k\,T}{[{}^{200}_{200}]}\left\{ 1 - \frac{2[{}^{200}_{021}]^2}{[{}^{200}_{200}]([{}^{021}_{021}]+[{}^{021}_{022}])} - \frac{[{}^{200}_{023}]^2}{[{}^{200}_{200}][{}^{023}_{023}]}\frac{1}{1+\alpha'^2} \right\}^{-1} \qquad (10)$$

where

$$\alpha' = a[{}^{023}_{023}]^{-1} = \frac{k\,T}{5}\left\langle \frac{\mathcal{N}(\mathcal{N}+1)(2\,\mathcal{N}-1)(2\,\mathcal{N}+3)}{2\,\mathcal{N}+1} \right\rangle_0 \frac{n^2}{[{}^{023}_{023}]}\frac{c}{p}$$

with $\mathcal{N}$ the magnitude of $\mathbf{N}$, i. e., the operator N^2 has the eigenvalues $\mathcal{N}(\mathcal{N}+1)$. A more detailed discussion of the validity of the approximations utilized in obtaining the above result can be found in ref. [5].

Diagonal square bracket integrals (diagonal collision integrals) can be expressed as inverse times characteristic of certain relaxation processes occurring the gas. For example, $[{}^{200}_{200}]$ is related to the mean-free-time which characterizes the shear viscosity coefficient η_0 in the main or, more explicitly, $n^{-1}[{}^{200}_{200}] \equiv \tau_{\text{free}}^{-1}$: this collision bracket can be rather well approximated by its elastic value, a simple Ω-integral [11]. The diagonal square bracket integrals $[{}^{021}_{021}]$ and $[{}^{023}_{023}]$ are, on the other hand, zero for purely elastic collisional processes. In particular, $[{}^{021}_{021}]$ can be related to the time scale over which

---

[10] This notation is one in which the numbers "ijk" represent the ranks i and j of the irreducible tensors in $\mathbf{W}$ and $\mathbf{N}$, respectively, in the expansion term while k represents the appropriate combination of projection operators; the upper row indicates the expansion term brought in when forming the scalar product in the variational procedure or moment method and the lower row indicates the expansion term upon which the collision operator acts.

[11] S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases, Cambridge University Press, London 1952. — J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., New York 1954.

the anisotropy in angular-momentum-space will be destroyed by an external field: it is, in fact, just a matching of the angular momentum precession frequency caused by the external magnetic field to the frequency defined by $n^{-1}\left[\begin{smallmatrix}021\\021\end{smallmatrix}\right] \equiv \tau_{inel.}^{-1}$ which is characteristic of the Senftleben effect for the shear viscosity, i. e., it determines the value on the H/p axis at which a longitudinal effect reaches half its saturation value. The time scale defined by $n^{-1}\left[\begin{smallmatrix}023\\023\end{smallmatrix}\right] = \tau_{inel.}'^{-1}$ can be, and quite probably is, rather different from that just discussed.

From such a point of view, it is perhaps illuminating to rewrite Eq. (10) as

$$\eta_0 = \eta_{iso}\left\{1 - \frac{2\left[\begin{smallmatrix}200\\021\end{smallmatrix}\right]^2}{\left[\begin{smallmatrix}200\\200\end{smallmatrix}\right]\left(\left[\begin{smallmatrix}021\\021\end{smallmatrix}\right]+\left[\begin{smallmatrix}021\\022\end{smallmatrix}\right]\right)} - \frac{\left[\begin{smallmatrix}200\\023\end{smallmatrix}\right]^2}{\left[\begin{smallmatrix}200\\200\end{smallmatrix}\right]\left[\begin{smallmatrix}023\\023\end{smallmatrix}\right]}\frac{1}{1+(\omega_{sr}\tau_{inel.}')^2}\right\}^{-1} \tag{11}$$

where $\eta_{iso} = -\frac{1}{2}n^2 k T\left[\begin{smallmatrix}200\\200\end{smallmatrix}\right]^{-1}$ is the isotropic value of η_0 and ω_{sr} is proportional to c in frequency units. From the form of Eq. (11), it is already apparent that the final term within the curly brackets describes a dispersion-like behaviour. The only quantity which can be freely varied here is the pressure: the contribution arising from this term is maximal for the limit $p \to \infty$ and zero for the limit $p \to 0$, reaching one half the maximal value for an intermediate pressure which is such that $\omega_{sr}\tau_{inel.}'$ is unity.

A crude estimate of the pressure region where this behaviour can be seen can be made in the following way. It has been shown in ref. [5] that the collision bracket $\left[\begin{smallmatrix}023\\023\end{smallmatrix}\right]$, because of its structure, can be expected to be smaller than $\left[\begin{smallmatrix}021\\021\end{smallmatrix}\right]$ and that it should be not unreasonable to estimate it to have between 10% and 1% of the value of the former quantity. This merely amounts to a time-scale argument and is not unprecedented: it is rather well known that even for the same collision brackets, different collisional processes which have widely different time scales can occur, the standard example of this being H_2 for which reorientation collisions and energetically inelastic collisions occur on time scales which are separated by a factor of ten. Now, assuming $\left[\begin{smallmatrix}021\\021\end{smallmatrix}\right]$ to be of the same order of magnitude as its equivalent square bracket integral for CO_2, $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]$, for which an estimate can be made from the characteristic position on the H/p axis at half-height of the Senftleben-Beenakker effect for the shear viscosity [12], as $(n^{-2}\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right])_{CO_2} \approx -6.25 \times 10^{-5}$ cm^3 s^{-1}, $n^{-2}\left[\begin{smallmatrix}023\\023\end{smallmatrix}\right]$ can be estimated to lie between -6.25×10^{-6} and -6.25×10^{-7} cm^3 s^{-1}. For a coupling constant of 1 GHz, a simple order-of-magnitude calculation results in the characteristic pressure range lying around 20 cm Hg to 200 cm Hg. As to the size of the effect, the same arguments which were applied to $\left[\begin{smallmatrix}023\\023\end{smallmatrix}\right]$ would imply that the off-diagonal collision bracket lies between the full value for and 10% of $\left[\begin{smallmatrix}200\\021\end{smallmatrix}\right]$. This leads to relative changes in η_0 of the order of 1% to 1‰ for a gas having a Senftleben effect of about 1%. Although this is rather small, it should be within the range of modern measuring techniques and it could be used to obtain information regarding collision brackets not easily extracted from other measurements. Such a pressure effect is more interesting as a matter of principle in that even in the dilute gas regime, not all polyatomic molecules have rigorously density-independent transport coefficients. As will be seen in the ensuing section, the class of such polyatomic molecules can be quite large. Note, however, that in the case of measurements of the Senftleben effects, the leading term (unity) in Eq. (10) is no longer present and hence the extra pressure dependence to be found in such experiments can be expected to be rather marked.

3. Discussion

It will be clear from the foregoing sections that the Senftleben effects for paramagnetic gases will also show a pressure dependence and roughly in the same pressure range. This problem has been treated quite generally for $^2\Sigma$ molecules [5] and even an explicit calculation of the thermal conductivity effect for a certain model has been undertaken [6]. The behaviour found for $-\Delta\lambda_\perp/\lambda_0$ in ref. [6] was as follows: at some intermediate pressure, the effect first increases with increasing field as a normal dispersion-like curve, reaches a maximum at higher fields and goes down to a very small saturation value. At very low pressures, the curve has the normal diamagnetic shape while at higher pressures, the maximum becomes smaller and finally disappears. This is illustrated in the figure where

$$\vartheta = \frac{n\,\gamma_s\,H}{15} \left\langle \frac{\mathcal{N}(\mathcal{N}+1)^2(2\mathcal{N}-1)^2(2\mathcal{N}+3)}{(2\mathcal{N}+1)^3} \right\rangle_0 \cdot (\begin{bmatrix}021\\021\end{bmatrix}+\begin{bmatrix}021\\022\end{bmatrix})^{-1},$$

γ_s being the gyromagnetic ratio of the molecules in the gas and H the magnitude of the magnetic field.

A simple physical picture similar to that for diamagnetic gases can be constructed in order to explain this behaviour. It will be recalled that in the diamagnetic case, there is an anisotropy in angular momentum-space caused by the collisional coupling of linear and angular momenta and by the macroscopic gradient responsible for the transport phenomenon. This anisotropy results in a (small) contribution to the field-free transport coefficient concerned. In placing the system in a constant homogeneous magnetic field, the angular momentum anisotropy is partially destroyed by the precession caused by the field: it is seldom totally destroyed because the field is unable to attack the anisotropy contribution corresponding to the projection of the angular momentum along the field axis. In the case of paramagnetic $^2\Sigma$ molecules, there is a small anisotropy in the total angular momentum ($\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}$) space: this is still created by the collisional coupling of the linear and (nuclear rotational) angular momenta and is communicated into the total angular momentum space by the spin-rotation coupling. The applied field causes a precession of the electronic spin which in turn, again through the spin-rotation coupling, partially destroys not only the $\boldsymbol{S}$-space anisotropy but also the $\boldsymbol{N}$-space anisotropy, thus causing a rather large (i. e., normal diamagnetic) end result. At somewhat higher field strengths, however, the electronic spin and nuclear rotational angular momenta become decoupled (i. e., they begin to precess independently) and, if the field is not sufficiently high to be causing a significant precession of $\boldsymbol{N}$ between two successive collisions, the anisotropy in $\boldsymbol{N}$ space is restored and the effect can return nearly to its field-free value (with only that anisotropy corresponding to $\boldsymbol{S} - S_H \hat{\boldsymbol{H}}$ being destroyed). At still higher fields, the $\boldsymbol{N}$-anisotropy is again partially destroyed through precession of $\boldsymbol{N}$ itself. For low enough pressures, no such dramatic behaviour will occur because the $\boldsymbol{N}$-anisotropy has already been destroyed by the precession of $\boldsymbol{N}$ before a field strength high enough to decouple $\boldsymbol{N}$ and $\boldsymbol{S}$ has been reached. The return of the saturation values to nearly the original saturation effect is not

seen in the figure because the computer solution has not been taken far enough to show this. The final saturation value is still slightly pressure dependent; at low pressures it has the same value as reached in the figure for $\alpha = 10\,(\alpha = \frac{1}{2}\,\alpha'\begin{bmatrix}023\\023\end{bmatrix}\{\begin{bmatrix}021\\021\end{bmatrix} + \begin{bmatrix}021\\022\end{bmatrix}\}^{-1})$ while it is slightly higher at higher pressures (the difference is of the order of a few percent).

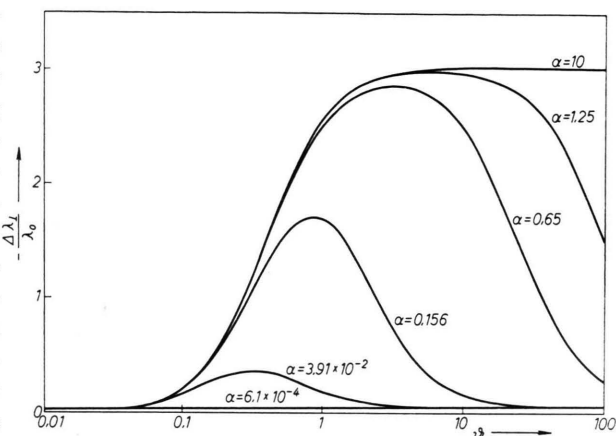Fig. 1. The relative change $-\Delta\lambda_\perp/\lambda_0$ (of the thermal conductivity in the presence of a magnetic field) for a gas of $^2\Sigma$ molecules for various pressures. The parameters α and ϑ are defined in the text; this figure contains the same information as in Fig. 2 of ref. [6] but is plotted in a different way.

The behaviour of the field-free effect will not be nearly as dramatic as that in the field and will be essentially that described in § 2 following Eq. (11).

Finally, it is worth discussing in slightly more detail the types of molecules for which density dependence in the field-dependent and in the field-free effects can be expected. Paramagnetic $^2\Sigma$ molecules have been treated here in detail since they offer the simplest theoretically tractable example. It is clear that their nonlinear polyatomic analogues, $^2A_1$ and $^2B_1$ molecules, of which NO_2 and ClO_2 are the most prominent examples, will show the same behaviour. In fact, TORWEGGE's measurements [13] for NO_2 corroborate this conclusion even though his field strengths did not allow the full saturation effect to be achieved.

For a gas of $^2\Pi$ molecules, the dominant term in the internal state Hamiltonian is that describing the spin-orbit coupling (corresponding to Russell-Saunders coupling in atomic spectroscopy). As the spin-orbit coupling energy is of the order of kT at room temperature, the characteristic pressure region

[13] H. TORWEGGE, Ann. Phys. Leipzig 33, 459 [1938].

Form of Coupling	Examples	Typical Level Splitting (GHz)	Pressure Effect Expected (yes or no)	Experimentally Detected Pressure Depend. in Field Effects
spin-rotation	CN ($^2\Sigma$)	0.3[a]	yes	—
	NO$_2$ ($^2A_1$)	5.0[b]	yes	yes[c]
	ClO$_2$ ($^2B_1$)	1.3[d]	yes	—
	O$_2$ ($^3\Sigma$)	1.0[e]	yes	yes[f]
pseudo-quadrupolar	O$_2$ ($^3\Sigma$)	59.4[e]	yes	—
spin-orbit	NO ($^2\Pi$)	3.7×10^3[g]	no	no[h]
	ClO ($^2\Pi_i$)	-8.5×10^3[i]	no	—
hindered internal rotation	CH$_3$OH	25[j]	yes	yes[k]
	CH$_3$NO$_2$	30[j]	yes	—
Inversion	NH$_3$	23.8[j]	yes	yes[l]
	ND$_3$	1.6[j]	yes	yes[l]
Strongly asymmetric top (polar)	C$_4$H$_4$S	—	yes	yes[k]
	(CH$_3$)$_2$CO	—	yes	—

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Table 1. Typical Couplings Giving Rise to Pressure Effects.

over which the pressure effects described in this paper would be expected to occur is around several hundred atmospheres. Such pressures are well beyond the dilute gas regime; at such pressures the

ordinary density effects from triple and higher multiple-particle collision effects will be much greater than that due to internal state effects. At ordinary pressures in the dilute gas regime, therefore, no special behaviour should be expected for such molecules. Typical examples of $^2\Pi$ molecules are ClO and NO and, indeed, measurements of the Senftleben effects for NO have shown no deviations from the H/p law [13, 14].

Oxygen, with a $^3\Sigma$ ground electronic state should also show special behaviour in that the spin-rotation coupling constant there is [15] 1 GHz so that there should be a weak pressure dependence in the range from a few cm Hg to about 1 atm. This has been observed in the transverse viscosity measurements [16, 17] for O$_2$ and has a behaviour consistent with the ideas presented here. A further pressure dependence should be seen at pressures around 10 atm due to the so-called pseudo-quadrupolar coupling term which has a coupling constant of [15] 60 GHz. Other characteristic internal state couplings which should give observable pressure effects are listed for convenience in Table 1 together with a few typical molecules to be found in each class.

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