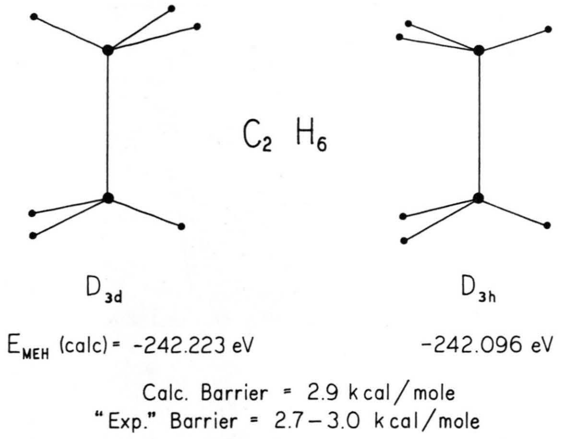

Fig. 10. The potential barrier in C_2H_6.

to those involving π bonds as well. It is our contention that the constants determined and used in this investigation are universal to all the hydrocarbons, be they aliphatic or aromatic. Furthermore, we believe that the technique as used in the determination of the atomization energies and stable configurations stands unique in its class of semi-empirical calculations.

Be that as it may, lest we mislead the reader with over-enthusiasm, we would like to stress that our methodology of estimating dissociation energies from the calculated atomization energies is not expected, because of its crude approximations, to be universally applicable. There is reason to believe, however, that the methodology has a greater chance of applicability whenever the ordinary extended Hückel calculation suggests a stable configuration and whenever nonbonding orbitals are not involved.

We certainly agree that many of our assumptions will not, and indeed cannot, pass the test of rigor. But then, why should one expect more rigor from the variants of the Hückel method when such rigor is not found in the Hückel method itself?

On the Senftleben-Beenakker Electric Effect in Gaseous Ammonia

A. C. Levi and G. E. Tommei

Istituto di Scienze Fisiche dell'Università and Gruppo Nazionale di Struttura
della Materia del C.N.R., Genova, Italy

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The viscosity of gaseous ammonia in the presence of a static homogeneous electric field is calculated using the Waldmann-Snider equation. Special attention is paid to the field dependence of the effect which is strongly influenced by molecular inversion. The latter causes a coupling of tensors of different rank in $\boldsymbol{J}$ in the expansion of the distribution matrix, thereby leading to an infinite set of equations which is solved numerically by a limiting procedure. The effect has a complicated dependence on pressure p and field E but to a good approximation turns out to depend on E/p at pressures high with respect to an inversion pressure (about 5 atm for NH_3, 300 torr for ND_3) and, in agreement with the experiments, on E^2/p at low pressures.

Introduction

Recently, Senftleben-Beenakker (SB) effects[1] (i.e. changes in the transport coefficients due to the presence of external fields) have been measured in ammonia[2,3]. The viscosity of ammonia is remarkable in that it shows an *increase* in the presence of both a magnetic[2] and an electric field[3]. This is an exception, since the viscosity of all other gases measured so far decreases when a field is applied. Moreover, the viscosity of ammonia in an electric field is a function of E^2/p (where p is the pressure) to a good approximation, in contradistinction to all other gases of symmetric top molecules[4] whose viscosity is a universal function of E/p. The thermal conductivity shows a decrease, but the field dependence seems to be similar to that of viscosity[3]. A comparison between NH_3 and

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Reprint requests to Dr. G. E. Tommei, Istituto di Scienze Fisiche, Viale Benedetto XV, 5-16132 Genova (Italy).

[1] J. J. M. Beenakker and F. R. McCourt, Ann. Rev. Phys. Chem. **21, 47** [1970].

[2] J. Korving, Physica **46**, 619 [1970].

[3] F. Tommasini, A. C. Levi, and G. Scoles, Z. Naturforsch., to be published; J. J. de Groot, C. J. N. van den Meijdenberg, and J. J. M. Beenakker, to be published.

[4] F. Tommasini, 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].

ND_3 shows that the latter saturates at much lower fields, but has a somewhat smaller saturation effect[3].

The present work deals with the field dependence of the effect. The theory is not simple because, as will be seen, the internal Hamiltonian of ammonia contains two terms (the inversion energy and the interaction with the external field) which do not commute with each other. Similar problems arise for linear molecules which might be treated along similar lines (however, the transport properties of such gases do not change appreciably before electrical breakdown takes place). The problems concerning the sign and size of the effect are much more difficult, and will be discussed only superficially here.

In § I the properties of the ammonia spectrum will be recalled, and a suitably simplified picture proposed to take into account the aspects relevant to the present problem. In § II the inversion quasi-degeneracy together with the degeneracy connected to the sign of the quantum number K will be treated by means of four Pauli-like matrices, and the kinetic theoretical problem will be formulated on the basis of the Waldmann-Snider equation[5, 6]. In § III the viscosity of ammonia will be studied, treatable approximations introduced and an infinite set of equations obtained. The numerical solution of the latter will be described in § IV. Finally, § V will be devoted to a comparison with the experimental data and to discussion.

I. Treatment of the Ammonia Molecule

The ammonia molecule, NH_3, can be considered in two ways. For very short times ($\ll 10^{-10}$ s) it has the shape of a depressed pyramid, belongs to the symmetry group C_{3v} and has a dipole moment of about 1.47 debijes[7] directed along the figure axis. For longer times, however, an inversion of the pyramid takes place, with an inversion frequency of 23.8 GHz[8]: the resulting molecule has therefore the shape of a flattish octahedron, belongs to the symmetry group D_{3h} and has no dipole moment. The reason why the two pictures are not contradictory is, of course, that the inversion frequency is extremely low in comparison to the normal vibration frequencies (the vibrational frequency for the vertical mode, ν_2, is 28500 GHz[9], i.e., there are about 1200 vibrations per inversion).

In the case of the dilute gas the relevant time is the time of flight between two collisions and inversion must be taken into account. In terms of temperature, the inversion energy is equivalent to 1.14 °K while the vibration quantum of the vertical mode is equivalent to 1430 °K: hence at room temperature the inversion doublet is in complete thermal equilibrium while only a few percent of the molecules are vibrationally excited. For heavy ammonia, ND_3, the inversion frequency is much lower, $\nu_i = 1.6$ GHz[8] (equivalent to .08 °K), while the vibrational frequency for the vertical mode is 22400 GHz[9] (equivalent to 1100 °K); for this species the number of vibrations per inversion is much larger: 14000.

The rotational states of NH_3 are those of a strongly oblate symmetric top and can be described with three quantum numbers J, K, M (the energy being independent of M and of the sign of K). The statistical weight of a state depends strongly on whether K is a multiple of 3 or not. In fact, NH_3 consists of two separate species, A-ammonia which always stays in states with K a multiple of 3 and E-ammonia which never goes to such states. The two species are equally abundant. For ND_3 a similar situation holds, except that $\frac{11}{27}$ of the molecules belong to species A and $\frac{16}{27}$ to species E[9]. In the following, however, these features will be mostly neglected since they hardly affect the rotational averages. Some effects that these selection rules may have will be discussed in Section V.

The inversion frequency depends on the rotational state: the frequency 23.8 GHz corresponds to $J = K = 0$; for higher quantum numbers the frequency ranges from 16 to 40 GHz but is still centred around 24 GHz at room temperature. The inversion doublet can be described in either of two representations. In the first representation the basis is formed by two states, $|\text{up}\rangle$ and $|\text{down}\rangle$, such that the nitrogen atom stays respectively above and below the plane of the hydrogens, and

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[5] L. Waldmann, Z. Naturforsch. **12a**, 660 [1957].

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

[7] Handbook of Chemistry and Physics, 48th Edition, The Chemical Rubber Co., Cleveland 1967.

[8] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill Book Company, New York 1955.

[9] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Co., Princeton 1945.

the molecule can be pictured as an upward, resp. downward, pyramid. In the second representation the basis is formed by the even and odd eigenstates

$$|+\rangle = \frac{1}{\sqrt{2}}\,(|\mathrm{up}\rangle + |\mathrm{down}\rangle);$$
$$|-\rangle = \frac{1}{\sqrt{2}}\,(|\mathrm{up}\rangle - |\mathrm{down}\rangle). \tag{1}$$

The latter are (as far as inversion is concerned) the eigenstates of the Hamiltonian; the first representation, however, is preferable from the pictorial point of view. In the present paper, reference to a specific representation will be hardly necessary.

Since the three protons (resp. deuterons) are indistinguishable, allowance should be made for their identity by restricting the wave function to be antisymmetric (resp. symmetric) in the exchange of any two of them. This leads to wave functions, which do not correspond to a fixed K but rather are linear combinations of $|K\rangle$ and $|-K\rangle$ with coefficients depending on the nuclear spins[8]. The different forms that such linear combinations take, according to whether K is a multiple of 3 or not, causes the difference between A-ammonia and E-ammonia. The states are restricted by the statistics to a subspace $\boldsymbol{P}$ of the total space $\boldsymbol{H}$ of formal wave functions. An operator A will be called physical if it maps $\boldsymbol{P}$ into itself. In the next section some non-physical operators will be introduced, but only physical operators will appear in the working formulae.

II. Kinetic Theory

As is usual, the non-equilibrium behaviour of the gas is described by the one-particle distribution matrix f. This is a matrix operating on the internal states of a molecule and at the same time a function of the momentum $\boldsymbol{p}$ depending on the position $\boldsymbol{x}$ and time t. If the gas is in an isotropic state (for example in equilibrium without external fields) the distribution matrix is diagonal and behaves as the identity matrix upon each separate degenerate multiplet. In the general case f is still diagonal with respect to those quantum numbers (J, $|K|$) which define the separation between the multiplets, but is non-diagonal inside the multiplets. Hence the anisotropic behaviour of f is closely connected to the degeneracies and quasi-degeneracies (two states are quasi-degenerate if their separation times the mean free time τ_{free} between two collisions is comparable with $\hbar$ or smaller) of the internal energy levels[10].

The space degeneracy connected to M is the same as for linear molecules in a magnetic field and gives rise to the same non-diagonal elements in the distribution matrix. This is, as usual, the main reason for the existence of the SB effect: when the distribution matrix is expanded in natural tensors in $\boldsymbol{J}$, the coefficients vary with the field in such a way as to make the matrix diagonal in M at high fields.

Next, the degeneracies due to the sign of K, to nuclear spin and to inversion, are to be taken into account. If the identity of the protons were neglected, these degeneracies should be considered separately. The first could be described by three matrices ϱ_i ($i = 1, 2, 3$) with the properties

$$\varrho_1|K\rangle = |-K\rangle, \qquad \varrho_2|K\rangle = i\,K\,|-K\rangle,$$
$$\varrho_3|K\rangle = K\,|K\rangle. \tag{2}$$

For identical nuclei these operators are in general non-physical. The degeneracy due to nuclear spin will be neglected in the following (although the fields lift the degeneracy) because the nuclear spin is practically uncoupled from rotation and does not affect the collisions. Finally, the inversion doublet may be treated in a similar way to the sign of K, by introducing three Pauli matrices σ_l ($l = 1, 2, 3$) as follows:

$$\sigma_1|p\rangle = p\,|p\rangle, \qquad \sigma_2|p\rangle = i\,p\,|-p\rangle,$$
$$\sigma_3|p\rangle = |-p\rangle \tag{3}$$

where the parity quantum number p, taking the values ± 1 in the $|\pm\rangle$ state, has been used. The matrices σ_l have been written in such a way as to take the Pauli form in the (up, down) representation. Now the matrix σ_1 is physical, but σ_2 and σ_3 are nonphysical since they cause the symmetry of the state to change. The products $\varrho_3\sigma_2$ and $\varrho_3\sigma_3$ are physical, however. Thus it is convenient to introduce a set of four matrices α_i ($i = 0, \ldots, 3$):

$$\alpha_0 = 1, \quad \alpha_1 = \sigma_1, \quad \alpha_2 = \varrho_3\,\sigma_2, \quad \alpha_3 = \varrho_3\,\sigma_3 \tag{4}$$

with the commutation rules $[\alpha_1, \alpha_2] = 2\,i\,\alpha_3$, $[\alpha_2, \alpha_3] = 2\,i\,J_\zeta{}^2\,\alpha_1$, $[\alpha_3, \alpha_1] = 2\,i\,\alpha_2$, $[\alpha_i, \alpha_j]_+ = 0$ for $i, j \neq 0$.

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[10] L. Waldmann, in Statistical Mechanics of Equilibrium and Nonequilibrium (ed. Meixner), North-Holland Publ. Co., Amsterdam 1965.

These are physical and allow a complete description of the ammonia inversion doublet (including the sign of K) when there is no nuclear spin polarization. The only remaining effect of nuclear spin is of course to give double weight to those states where K is a multiple of 3 (but non-zero), i.e. to fix the relative concentrations of A- and E-ammonia.

Thus, the distribution matrix f must be a linear combination of the four α-matrices, the coefficients depending still on the angular momentum $\boldsymbol{J}$, on the square of its projection on the figure axis $J_\zeta{}^2$ (with eigenvalues K^2), and of course on the c-numbers $\boldsymbol{p}$, $\boldsymbol{x}$ and t.

The distribution matrix obeys the Waldmann-Snider equation[5,6]

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\cdot\nabla f = C(f,f) - \frac{i}{\hbar}\,[\mathscr{H}_{\text{int}}, f] \tag{5}$$

in which C is the bilinear collision superoperator

$$C(A,B) = (2\pi)^4\,\hbar^2\,\mathrm{tr}_2 \int \mathrm{d}\boldsymbol{p}_2 \times \left\{ \int t^{\mathrm{g}}_{\mathrm{g}'}\,A'B'_2\,t^{\mathrm{g}\dagger}_{\mathrm{g}'}\,\delta(E)\,\mathrm{d}\boldsymbol{p}' + \frac{1}{2\pi i}\,(t^{\mathrm{g}}_{\mathrm{g}}\,A B_2 - A B_2\,t^{\mathrm{g}\dagger}_{\mathrm{g}}) \right\} \tag{6}$$

where the subscript 2 denotes the partner in a binary collision, tr_2 designates the trace over its internal states, $t^{\mathrm{g}}_{\mathrm{g}'}$ and $t^{\mathrm{g}\dagger}_{\mathrm{g}'}$ are the matrix elements (in relative momentum space) of the transition operator t and its adjoint $t^\dagger$, a prime means that a quantity is a function of the initial momenta $(\boldsymbol{p}', \boldsymbol{p}_2')$ and $\delta(E)$ expresses the conservation of total energy in the collision.

$$\mathscr{H}_{\text{int}} = \mathscr{H}_{\text{rot}} + \mathscr{H}_{\text{inv}} + \mathscr{H}_{\text{field}} \tag{7}$$

is the internal state Hamiltonian:

$\mathscr{H}_{\text{rot}}$ stands for the rotational Hamiltonian, i.e.

$$\mathscr{H}_{\text{rot}} = \tfrac{1}{2}\,\hbar^2\,I_A^{-1}\,\{J^2 + (I_A/I_C - 1)\,J_\zeta{}^2\} \tag{8}$$

and $\mathscr{H}_{\text{inv}}$ and $\mathscr{H}_{\text{field}}$ stand respectively for the inversion and the field Hamiltonian.

In the field-free case, f may be assumed diagonal in J and $|K|$. In fact, considering the order of magnitude of the terms at the right-hand side of Eq. (5), if

$$E_\alpha - E_\beta \gg (\hbar/\tau_{\text{free}})\,, \tag{9}$$

where α and β are two stationary states, then $f_{\alpha\beta} \ll f_{\alpha\alpha}$. If $E_{\alpha,\beta}$ are rotational energies, condition (9) is verified up to 10 atmospheres at least and f is diagonal. In the presence of a field if $\mathscr{H}_{\text{field}}$ commutes with $\mathscr{H}_{\text{rot}}$ this is still true. Although in the electric case $\mathscr{H}_{\text{field}}$ does not commute in general with $\mathscr{H}_{\text{rot}}$, the part of $\mathscr{H}_{\text{field}}$ which is off-diagonal in J becomes important only at fields of several million V/cm. Hence $\mathscr{H}_{\text{field}}$ will be assumed to commute with $\mathscr{H}_{\text{rot}}$ and to have the form

$$\mathscr{H}_{\text{field}} = -\,\mathrm{d}E\,J^{-2}\,\boldsymbol{e}\cdot\boldsymbol{J}\alpha_3 \tag{10}$$

where d is the dipole moment, E and $\boldsymbol{e}$ are the magnitude of the electric field and the unit vector along its direction and α_3 has been written in place of J_ζ according to the notation of the present article. Thus, f will be diagonal in J and $|K|$ even in the presence of the field.

As far as inversion is concerned, $\mathscr{H}_{\text{inv}}$ will be taken to have the form

$$\mathscr{H}_{\text{inv}} = -\,\tfrac{1}{2}\,\hbar\,\omega_i\,\alpha_1 \tag{11}$$

(the minus sign implies that in the lower inversion state the vibrational wave function is even). Actually the present picture is oversimplified since the inversion frequency, as noted above, depends on the rotational state. Such inversion-rotation coupling will be neglected in the following. This can be justified by observing that the inversion lines with a frequency lower than 20 or higher than 30 GHz are very weak. For $\nu_i = \omega_i/2\pi$ the value 23.786 GHz has been chosen. This is obtained from a fit of the experimental values letting $J = K = 0$ (although symmetry considerations exclude the lower inversion state for this case) but also represents an average of the experimental frequencies weighted with the corresponding intensities[8] (Fig. 1). The presence of $\mathscr{H}_{\text{inv}}$ does not affect the diagonality of f with respect to J and $|K|$; as for p, in the field-free case the energy difference between two inversion states satisfies condition (9) when the pressure is sufficiently low (a few torr),

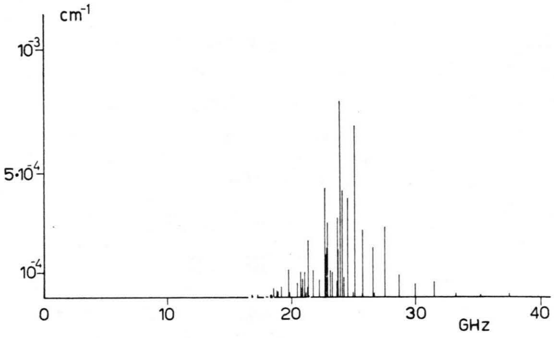

Fig. 1. Observed NH_3 inversion lines and corresponding intensities. The mean frequency is about 24 GHz.

so that f could be assumed to be diagonal also in p. But, when an electric field is present, since $[\mathscr{H}_{\text{inv}}, \mathscr{H}_{\text{field}}] \neq 0$, p is no longer a good quantum number and f cannot be diagonal in p even at low pressures.

In the approximation made, where f is diagonal in J and $|K|$, $\mathscr{H}_{\text{rot}}$ and f commute so that Eq. (5) may be rewritten

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \nabla f = C(f, f) - \frac{i}{\hbar} [\mathscr{H}_{\text{inv}} + \mathscr{H}_{\text{field}}, f] . \quad (12)$$

If the inhomogeneities are not too strong and the pressure is not too low (typically for pressures higher than 10^{-1} torr) a hydrodynamic description is valid and the Waldmann-Snider equation can be solved by a Chapman-Enskog procedure. In such a treatment f depends on $\boldsymbol{x}$ and t only via the macroscopic quantities n (density), T (temperature) and $\boldsymbol{v}_0$ (stream velocity). A Maxwellian $f^{(0)}$ describes local equilibrium, $C(f^{(0)}, f^{(0)}) = 0$, and f differs from $f^{(0)}$ by a small amount:

$$f = f^{(0)} (1 + \Phi) \quad (13)$$

where the perturbation Φ is a linear combination of temperature and velocity gradients. Here the electric field has been assumed to be so low as to affect only Φ but not $f^{(0)}$; this amounts to neglecting the electric polarization of the gas in equilibrium: indeed, it is easy to see that such polarization is very weak at room temperature and has no influence on the transport properties.

III. The Shear Viscosity

Focusing the attention on the problem of shear viscosity, the temperature is assumed to be uniform and Φ takes the form

$$\Phi = - \mathbf{B} \cdot {}^2[\nabla \boldsymbol{v}_0]^{(2)} \quad (14)$$

where $[\nabla \boldsymbol{v}_0]^{(2)}$ is the symmetric traceless part of the velocity gradient tensor, and $\mathbf{B}$ only depends on microscopic variables, such as the angular momentum $\boldsymbol{J}$ or the reduced peculiar velocity

$$\boldsymbol{W} = (m/2kT)^{1/2} (\boldsymbol{p}/m - \boldsymbol{v}_0) . \quad (15)$$

The shear viscosity tensor is given by

$$\boldsymbol{\eta} = n k T \langle [\boldsymbol{W}]^{(2)} \mathbf{B} \rangle \quad (16)$$

where $[\ ]^{(l)}$ indicates the l-th rank natural tensor (symmetric and traceless in all pairs of indices) and $\langle\ \rangle$ the equilibrium average. The problem is of course to find $\mathbf{B}$, which is the solution of the Chapman-Enskog equation

$$- 2 [\boldsymbol{W}]^{(2)} = (\mathscr{C} + \mathscr{C}') \mathbf{B} . \quad (17)$$

Here $\mathscr{C}$ is the linearized Waldmann-Snider collision superoperator

$$\mathscr{C} A = f^{(0)-1} \{ C(f^{(0)} A, f^{(0)}) + C(f^{(0)}, f^{(0)} A) \} \quad (18)$$

and $\mathscr{C}'$ is the sum of the inversion superoperator $\mathscr{I}$ and the field superoperator $\mathscr{F}$:

$$\mathscr{C}' = \mathscr{I} + \mathscr{F} \quad (19)$$

where

$$\mathscr{F}_A = - \frac{i}{\hbar} [\mathscr{H}_{\text{inv}}, A] , \mathscr{I} A = - \frac{i}{\hbar} [\mathscr{H}_{\text{field}}, A] . \quad (20)$$

Eq. (17) is solved by a variational procedure. $\mathbf{B}$ is expanded in natural tensors constructed from the vectors $\boldsymbol{W}$ and $\boldsymbol{J}$, in polynomials depending on W^2, J^2 and $J_\zeta{}^2$ and in the four matrices α_i. However, not all possible terms are considered but only those which arise naturally in the problem. In the case of ammonia the situation is unfortunately very complicated since the inversion and field Hamiltonians do not commute with each other and this causes all possible ranks in $\boldsymbol{J}$ to be simultaneously present. Let now the various terms relevant for the expansion be discussed in detail.

First of all, the second rank tensor $[\boldsymbol{W}]^{(2)}$ must certainly be included since, because of orthogonality, it is the only term contributing to (16). Then terms not commuting with $\mathscr{H}_{\text{field}}$ must be present, otherwise no field effect would arise: these must contain $\boldsymbol{J}$ or the matrices α_i or both. Since experimentally the electric field effect[3] and the magnetic field effect[2] are about equal, it is reasonable to assume that the same terms are important in both cases. KORVING[2] has taken into account the terms $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$, $[\boldsymbol{J}]^{(2)}$ and $[\boldsymbol{J}]^{(2)}[\boldsymbol{W}]^{(2)}$. In the present work the last term will be discarded, since it behaves very much like $[\boldsymbol{J}]^{(2)}$ and is more complicated.

Assume then $\mathbf{B}$ to be given, in the absence of a field, by

$$\mathbf{B} = [\boldsymbol{W}]^{(2)}\, {}^2\underline{\mathscr{B}}^{200} + [\boldsymbol{J}]^{(2)}\, {}^2\underline{\mathscr{B}}^{020} + \boldsymbol{J}[\boldsymbol{W}]^{(2)}\, {}^3\underline{\mathscr{B}}^{210} \quad (22)$$

(where the first superscript in the coefficients refers to the rank in $\boldsymbol{W}$, the second to the rank in $\boldsymbol{J}$ and the third to the matrix α_i; no superscript for the polynomials will be needed in this work) and consider which additional terms are bound to arise in the presence of an electric field. For instance if the term $[\boldsymbol{J}]^{(2)}$ is present, commutation with the field Hamiltonian induces the presence of the term $\alpha_3[\boldsymbol{J}]^{(2)}$ (together with a whole series of terms obtained from multiplication of the latter term by polynomials in the internal energy[4]; these will be disregarded in this simplified, LMT-like[11] treatment). At this point, however, there arises an important difference between ammonia and ordinary symmetric tops, such as chloroform. For these gases only the field Hamiltonian contributes significantly to the commutator and this from $\alpha_3[\boldsymbol{J}]^{(2)}$ can only generate $[\boldsymbol{J}]^{(2)}$ back (apart from polynomials). In the case of ammonia, however, the inversion Hamiltonian, containing α_1, generates by commutation with $\alpha_3[\boldsymbol{J}]^{(2)}$ the new term $\alpha_2[\boldsymbol{J}]^{(2)}$. Then the field Hamiltonian can generate terms of different rank, such as $\alpha_1\boldsymbol{J}$ and $\alpha_1[\boldsymbol{J}]^{(3)}$, then α_2 and $\alpha_2[\boldsymbol{J}]^{(4)}$, then $\alpha_1[\boldsymbol{J}]^{(5)}$ and so on to infinity. Any $\boldsymbol{J}$-dependent term present in the field-free case will generate, in the presence of the electric field, terms of all ranks in $\boldsymbol{J}$. The situation is schematized in the form of genealogical trees in Fig. 2.

Hence, in the presence of an electric field, a self-consistent theory requires $\mathbf{B}$ to be put in the following form:

$$\begin{aligned}\mathbf{B} = {} & [\boldsymbol{W}]^{(2)} \cdot {}^{2}\mathbf{B}^{200} + \sum_{\substack{q=0\\ i=0,2,3}}^{\infty}{}' \alpha_i [\boldsymbol{J}]^{(2q)} \cdot {}^{2q}\mathbf{B}^{0,2q,i} \\ & + \sum_{q=0}^{\infty} \alpha_1 [\boldsymbol{J}]^{(2q+1)} \cdot {}^{2q+1}\mathbf{B}^{0,2q+1,1} \\ & + \sum_{\substack{q=0\\ i=0,2,3}}^{\infty} \alpha_i [\boldsymbol{J}]^{(2q+1)} [\boldsymbol{W}]^{(2)} \cdot {}^{2q+3}\mathbf{B}^{2,2q+1,i} \\ & + \sum_{q=0}^{\infty} \alpha_1 [\boldsymbol{J}]^{(2q)} [\boldsymbol{W}]^{(2)} \cdot {}^{2q+2}\mathbf{B}^{2,2q,1}\end{aligned} \tag{23}$$

where the prime indicates the absence of the term $i = q = 0$.

Eq. (17) permits to evaluate the coefficients of $\mathbf{B}$ by taking the scalar products with the terms contained in the development of $\mathbf{B}$:

$$(x, y) = n\langle x^\dagger y\rangle . \tag{24}$$

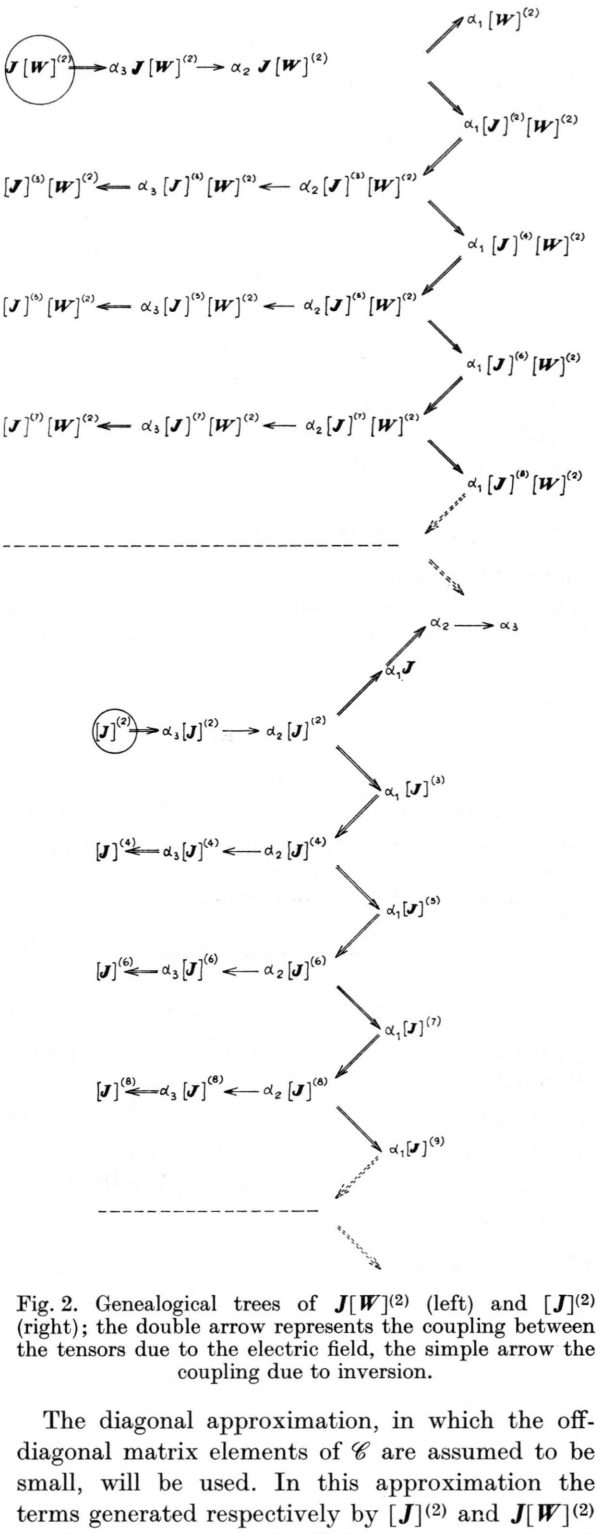

Fig. 2. Genealogical trees of $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ (left) and $[\boldsymbol{J}]^{(2)}$ (right); the double arrow represents the coupling between the tensors due to the electric field, the simple arrow the coupling due to inversion.

The diagonal approximation, in which the off-diagonal matrix elements of $\mathscr{C}$ are assumed to be small, will be used. In this approximation the terms generated respectively by $[\boldsymbol{J}]^{(2)}$ and $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ can be treated separately. Only the terms generated

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

by $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ will be considered in detail here because, as shown by KORVING[2], $[\boldsymbol{J}]^{(2)}$ gives a contribution about five times smaller than $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ to the saturation value; it must be observed at this point that no calculation of the saturation value will be attempted in this work. Considering only $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ and the terms generated from it, (23) reduces to:

$$\mathbf{B} = [\boldsymbol{W}]^{(2)} \cdot {}^{2}\mathbf{B}^{200} + \sum_{\substack{q=0\\ i=0,2,3}}^{\infty} \alpha_i [\boldsymbol{J}]^{(2q+1)} [\boldsymbol{W}]^{(2)} \cdot {}^{2q+3}\mathbf{B}^{2,\,2q+1,\,i} + \sum_{q=0}^{\infty} \alpha_1 [\boldsymbol{J}]^{(2q)} [\boldsymbol{W}]^{(2)} \cdot {}^{2q+2}\mathbf{B}^{2,\,2q,\,1}\,. \tag{25}$$

The coefficients $\mathbf{B}^{200}$ and $\mathbf{B}^{210}$ are present even in the absence of the field and can be split in the usual way into field-free and field-dependent parts as

$$\mathbf{B}^{200} = \underline{\mathscr{B}}^{200} + \mathfrak{B}^{200} \qquad \mathbf{B}^{210} = \underline{\mathscr{B}}^{210} + \mathfrak{B}^{210} \tag{26}$$

where $\mathfrak{B}^{200}$ and $\mathfrak{B}^{210}$ vanish in the absence of the field. The field-free quantities $\underline{\mathscr{B}}^{200}$ and $\underline{\mathscr{B}}^{210}$, occurring in Eq. (22), are isotropic tensors of the fourth and fifth rank respectively and can be written in the form:

$$\underline{\mathscr{B}}^{200} = \mathscr{B}^{200}\,\mathbf{E}^{(2)} \qquad \underline{\mathscr{B}}^{210} = \mathscr{B}^{210}\,\tilde{\mathbf{S}}^{(2)} \tag{27}$$

where $\mathbf{E}^{(q)}$ is the isotropic tensor of rank $2q$ which is symmetric and traceless in the first and second set of q indices[12], and $\tilde{\mathbf{S}}^{(q)}$ is defined as follows:

$$\tilde{S}^{(q)}_{i_1,\dots,i_q,k,j_1,\dots,j_q} = S^{(q)}_{i_1,\dots,i_q,j_1,\dots,j_q,k} = \sum_{s=1}^{q} E^{(q)}_{i_1,\dots,i_q,j_1,\dots,j_{s-1}j_{s+1},\dots,j_q\alpha}\,\mathscr{E}_{\alpha j_s k} \tag{28}$$

($\mathscr{E}$ is the Levi-Civita tensor).

These field-free coefficients satisfy the equations

$$-\,n\,\mathbf{E}^{(2)} = [200]\,\mathscr{B}^{200} + \genfrac{[}{]}{0pt}{}{200}{210} \cdot {}^{3}\tilde{\mathbf{S}}^{(2)}\,\mathscr{B}^{210}\,, \tag{29}$$
$$0 = \genfrac{[}{]}{0pt}{}{210}{200}\,\mathscr{B}^{200} + [210] \cdot {}^{3}\tilde{\mathbf{S}}^{(2)}\,\mathscr{B}^{210}$$

obtained by taking the scalar products with $[\boldsymbol{W}]^{(2)}$ and $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ as described above, where the collision brackets have been introduced as follows:

$$[x] = (x, \mathscr{C} x) \qquad \genfrac{[}{]}{0pt}{}{x}{y} = (x, \mathscr{C} y) \tag{30}$$

(in practice, a tensor is replaced in the collision brackets by a set of three numbers according to the same convention used for the $\mathbf{B}'$s). If the collision brackets have a simple tensorial nature, scalar brackets can be introduced; thus for example

$$[200] = [200]\,\mathbf{E}^{(2)}, \qquad \genfrac{[}{]}{0pt}{}{210}{200} = \genfrac{[}{]}{0pt}{}{210}{200}\,\tilde{\mathbf{S}}^{(2)}\,. \tag{31}$$

As for $[210]$, the situation is more complicated since this is a rather general isotropic tensor of the sixth rank. If, however, the spherical approximation is applied (no coupling between $\boldsymbol{W}$ and $\boldsymbol{J}$) then $[210]$ will take the form

$$[210]_{ijklmn} = [210]\,\delta_{kl}\,E^{(2)}_{ijmn}\,. \tag{32}$$

In the diagonal approximation the second term on the r.h.s. of the first Eq. (29) is neglected and the simple solution

$$\mathscr{B}^{200} = -\,n\,[200]^{-1}\,,$$
$$\mathscr{B}^{210} = n\,[200]^{-1}\,[210]^{-1}\genfrac{[}{]}{0pt}{}{210}{200} \tag{33}$$

is obtained.

Turning now to the field-dependent case, subtracting out the field-free equations and applying again the diagonal approximation, the following system of infinite coupled equations is obtained:

$$0 = [200] \cdot {}^{2}\mathfrak{B}^{200} + \genfrac{[}{]}{0pt}{}{200}{210} \cdot {}^{3}\mathfrak{B}^{210}\,, \qquad 0 = [210] \cdot {}^{3}\mathfrak{B}^{210} + \tfrac{1}{2}\,c_1 \cdot \mathscr{E} \cdot \boldsymbol{e} \cdot \mathbf{B}^{213}\,,$$
$$0 = [2\;\; q+1\;\; 0] \cdot {}^{q+3}\mathbf{B}^{2,\,q+1,\,0} + \tfrac{1}{2}\,c_{q+1}\,\mathbf{S}^{(q+1)} \cdot \boldsymbol{e} \cdot {}^{q+1}\mathbf{B}^{2,\,q+1,\,3} \qquad (q>0)\,,$$
$$0 = [2\;\; q+1\;\; 2] \cdot {}^{q+3}\mathbf{B}^{2,\,q+1,\,2} - c_{q+1}\,\mathbf{E}^{(q+1)} \cdot {}^{q+1} \cdot \boldsymbol{e}\,\mathbf{B}^{2,\,q,\,1} - \frac{c_{q+2}}{(q+2)(2q+3)}\,\boldsymbol{e} \cdot \mathbf{B}^{2,\,q+1,\,1} + \tfrac{1}{2}\,d_{q+1}\,\mathbf{B}^{2,\,q+1,\,3}, \tag{34}$$
$$-\tfrac{1}{2}\,c_1\,\mathscr{E} \cdot \boldsymbol{e} \cdot \underline{\mathscr{B}}^{210} = [213] \cdot {}^{3}\mathbf{B}^{213} + \tfrac{1}{2}\,c_1\,\mathscr{E} \cdot \boldsymbol{e} \cdot \mathfrak{B}^{210} - \tfrac{1}{2}\,d_1\,\mathbf{B}^{212}\,,$$
$$0 = [2\;\; q+1\;\; 3] \cdot {}^{q+3}\,\mathbf{B}^{2,\,q+1,\,3} + \tfrac{1}{2}\,c_{q+1}\,\mathbf{S}^{(q+1)} \cdot \boldsymbol{e} \cdot {}^{q+1}\,\mathbf{B}^{2,\,q+1,\,0} - \tfrac{1}{2}\,d_{q+1}\,\mathbf{B}^{2,\,q+1,\,2} \qquad (q>0),$$
$$0 = [201] \cdot {}^{2}\mathbf{B}^{210} + c_1\,\boldsymbol{e} \cdot \mathbf{B}^{212}\,,$$
$$0 = [2\;\; q\;\; 1] \cdot {}^{q+2}\mathbf{B}^{2,\,q,\,1} + c_q\,\mathbf{E}^{(q)} \cdot \boldsymbol{e}\,\mathbf{B}^{2,\,q-1,\,2} + \frac{c_{q+1}}{(q+1)(2q+1)}\,\boldsymbol{e} \cdot \mathbf{B}^{2,\,q+1,\,2}$$

in which q is an even integer, $c_q = \dfrac{\mathrm{d}E\,n}{\hbar}\,\dfrac{1}{2q+1}\left\langle \dfrac{J_\zeta{}^2}{J^2}\,\nu_q(J^2) \right\rangle$, $\quad d_q = n\,\omega_i\,\dfrac{1}{2q+1}\,\langle J_\zeta{}^2\,\nu_q(J^2)\rangle\,,$ (35, 36)

$$\nu_q(J^2) = [\boldsymbol{J}]^{(q)} \cdot {}^{q}[\boldsymbol{J}]^{(q)} = \frac{q\,!}{(2q-1)\,!!}\,\prod_{p=1}^{q}\,(J^2 - \tfrac{1}{4}\,p^2 + \tfrac{1}{4})\,. \tag{37}$$

[12] J. A. R. COOPE and R. F. SNIDER, J. Math. Phys. **1**, 1003 [1970].

Using now the projection operator technique, the tensorial system (34) may be transformed into a system of numerical equations. It is convenient to introduce the operators occurring in the system (34) as follows:

$$a\,\mathbf{T} = \boldsymbol{e}\cdot\mathbf{T}\,, \tag{38}$$

$$b\,\mathbf{T} = \mathbf{E}^{(q+1)}\cdot{}^{q+1}\boldsymbol{e}\,\mathbf{T}\,, \tag{39}$$

$$\mathscr{L}\,\mathbf{T} = \mathbf{S}^{(q)}\cdot\boldsymbol{e}\cdot{}^{q}\mathbf{T}\,. \tag{40}$$

a, b and $\mathscr{L}$ operate only on the first q indices of the tensor $\mathbf{T}$; a lowers and b raises the rank of $\mathbf{T}$ by one, while $\mathscr{L}$ leaves this rank unchanged and can be considered as the component of a vectorial operator $\underline{\mathscr{L}}$($-i\underline{\mathscr{L}}$ has the algebraic properties of angular momentum) in the field direction. Since the eigenvalues of $\mathscr{L}$ are im ($|m| \leqq q$), projection operators on the invariant subspaces of $\mathscr{L}$ can be introduced and $\mathscr{L}$ can be rewritten:

$$\mathscr{L} = i\sum_{m=-q}^{q} m\,\mathscr{P}^{(q,m)}\,. \tag{41}$$

The operators a and b commute with $\mathscr{L}$, hence their commutation rules with $\mathscr{P}^{(q,m)}$ are the following:

$$\begin{aligned} a\,\mathscr{P}^{(q,q)} &= a\,\mathscr{P}^{(q,-q)} = 0\,,\\ a\,\mathscr{P}^{(q,m)} &= \mathscr{P}^{(q-1,m)}\,a \quad \text{for} \quad |m| < q\,,\\ \mathscr{P}^{(q+1,q+1)}\,b &= \mathscr{P}^{(q+1,-q-1)}\,b = 0\,,\\ b\,P^{(q,m)} &= \mathscr{P}^{(q+1,m)}\,b \quad \text{for} \quad |m| \leqq q\,. \end{aligned} \tag{42}$$

a and b do not commute with each other. Their products are diagonal in the (q, m) representation:

$$\begin{aligned} a\,b\,\mathscr{P}^{(q,m)} &= \frac{q+1}{2q+1}\left\{1-\frac{m^2}{(q+1)^2}\right\}\mathscr{P}^{(q,m)}\,,\\ b\,a\,\mathscr{P}^{(q,m)} &= \frac{q}{2q-1}\left\{1-\frac{m^2}{q^2}\right\}\mathscr{P}^{(q,m)}\,. \end{aligned} \tag{43}$$

Using the operators a, b, $\mathscr{L}$ and applying the spherical approximation to the collision brackets $[2q+1\;i]$ $(i = 0, 2, 3)$ and $[2q\;1]$ the tensorial system (34) (apart from the first equation containing $\mathfrak{B}^{200}$, which is to be considered later) can be written:

$$\begin{aligned} 0 &= [210]\,\mathfrak{B}^{210} + \tfrac{1}{2}c_1\,\mathscr{L}\,\mathbf{B}^{213}\,,\\ 0 &= [2\;\;q+1\;\;0]\,\mathbf{B}^{2,q+1,0} + \tfrac{1}{2}c_{q+1}\,\mathscr{L}\,B^{2,q+1,3} \qquad (q>0)\,,\\ 0 &= [2\;\;q+1\;\;2]\,\mathbf{B}^{2,q+1,2} - c_{q+1}\,b\,\mathbf{B}^{2,q,1} - \frac{c_{q+2}}{(q+2)(2q+3)}\,a\,\mathbf{B}^{2,q+2,1} + \tfrac{1}{2}d_{q+1}\,\mathbf{B}^{2,q+1,3}\,,\\ -\tfrac{1}{2}c_1\,\mathscr{L}\,\underline{\mathscr{B}}^{210} &= [213]\,\mathbf{B}^{213} + \tfrac{1}{2}c_1\,\mathscr{L}\,\mathfrak{B}^{210} - \tfrac{1}{2}d_1\,\mathbf{B}^{212}\,,\\ 0 &= [2\;\;q+1\;\;3]\,\mathbf{B}^{2,q+1,3} + \tfrac{1}{2}c_{q+1}\,\mathscr{L}\,\mathbf{B}^{2,q+1,0} - \tfrac{1}{2}d_{q+1}\,\mathbf{B}^{2,q+1,2} \qquad (q>0)\,,\\ 0 &= [2\;\;0\;\;1]\,\mathbf{B}^{201} + c_1\,a\,\mathbf{B}^{212}\,,\\ 0 &= [2\;\;q\;\;1]\,\mathbf{B}^{2q1} + c_q\,b\,\mathbf{B}^{2,q-1,2} + \frac{c_{q+1}}{(q+1)(2q+1)}\,a\,\mathbf{B}^{2,q+1,2} \qquad (q>0)\,. \end{aligned} \tag{44}$$

The known term of such a set, containing $\underline{\mathscr{B}}^{210}$, has the tensorial properties of $\mathscr{L}\tilde{\mathbf{S}}^{(2)}$, hence is a linear combination of $\mathscr{P}^{(1,m)}\tilde{\mathbf{S}}^{(2)}$. The equations only contain, apart from scalar coefficients, the operators a, b, $\mathscr{L}$. As a consequence, any coefficient of rank $q+5$ must be a linear combination of the tensors $\mathscr{P}^{(q+1,m)}\,b^q\,\tilde{\mathbf{S}}^{(2)}$ with $|m| \leqq 1$. Thus:

$$\mathbf{B}^{2,q+1,i} = \sum_{-1}^{1}{}_{m}\,\xi^{2,q+1,i,m}\,\mathscr{P}^{(q+1,m)}\,b^q\,\tilde{\mathbf{S}}^{(2)} \qquad (i = 0, 2, 3;\ \text{not}\ i = q = 0)\,,$$

$$\mathbf{B}^{2,q,1} = \sum_{-1}^{1}{}_{m}\,\xi^{2q1m}\,\mathscr{P}^{(q,m)}\,b^{q-1}\,\tilde{\mathbf{S}}^{(2)} \qquad (q>0)\,,$$

$$\mathbf{B}^{2,0,1} = \xi^{2010}\,\tilde{a}\,\mathbf{S}^{(2)}\,, \qquad \mathfrak{B}^{210} = \sum_{-1}^{1}{}_{m}\,\xi^{210m}\,\mathscr{P}^{(1,m)}\,\tilde{\mathbf{S}}^{(2)}\,.$$

The numerical coefficients ξ's corresponding to a given m obey a separate system of equations:

$$\begin{aligned} 0 &= [2\;\;q+1\;\;0]\,\xi^{2,q+1,0,m} + \tfrac{1}{2}\,i\,m\,c_{q+1}\,\xi^{2,q+1,3,m}\,,\\ 0 &= [2\;\;1\;\;2]\,\xi^{212m} - c_1\,\xi^{201m}\,\delta_{0m} - \tfrac{1}{9}\left(1-\tfrac{1}{4}m^2\right)c_1\,\xi^{221m} + \tfrac{1}{2}d_1\,\xi^{213m}\,,\\ 0 &= [2\;\;q+1\;\;2]\,\xi^{2,q+1,2,m} - c_{q+1}\,\xi^{2q1m} - \frac{1}{(2q+3)^2}\left\{1-\frac{m^2}{(q+2)^2}\right\}c_{q+2}\,\xi^{2,q+2,1,m}\\ &\qquad + \tfrac{1}{2}d_{q+1}\,\xi^{2q+1,3,m} \qquad (q>0)\,,\\ -\tfrac{1}{2}\,i\,m\,c_1\,\mathscr{B}^{210} &= [213]\,\xi^{213m} + \tfrac{1}{2}\,i\,m\,c_1\,\xi^{210m} - \tfrac{1}{2}d_1\,\xi^{212m}\,, \end{aligned}$$

$$
\begin{aligned}
0 &= [2\ q+1\ 3]\,\xi^{2,q+1,3,m} + \tfrac{1}{2}\,i\,m\,c_{q+1}\,\xi^{2,q+1,0,m} - \tfrac{1}{2}\,d_{q+1}\,\xi^{2,q+1,2,m} \qquad (q>0),\\
0 &= [201]\,\xi^{2010} + c_1\,\xi^{2120},\\
0 &= [2\ q\ 1]\,\xi^{2q1m} + c_q\,\xi^{2,q-1,2,m} + \frac{1}{(2q+1)^2}\left\{1-\frac{m^2}{(q+1)^2}\right\} c_{q+1}\,\xi^{2,q+1,2,m} \qquad (q>0)
\end{aligned}
\tag{46}
$$

where the Eqs. (43) have been used.

IV. Numerical Computations

The next task is to solve the set of Eqs. (46) by numerical methods.

Writing $\xi^{2,q+1,0,m}$, $\xi^{2,q+1,3,m}$ and $\xi^{2,q,1,m}$ in terms of $\xi^{2,q+1,2,m}$ (this being the most convenient choice) the following system is obtained:

$$\alpha_0\,\xi_1 + \beta_0\,\xi_0 = i\,m\,f, \qquad \alpha_n\,\xi_{n+1} + \beta_n\,\xi_n + \gamma_n\,\xi_{n-1} = 0, \qquad n \geqq 1 \tag{47}$$

where

$$n = q/2 \qquad \text{and} \qquad \xi_n = \xi^{2,q+1,2,m}. \tag{48}$$

Furthermore,

$$\alpha_n = \frac{1}{(2q+3)^2(2q+5)^2}\cdot\left\{1-\frac{m^2}{(q+2)^2}\right\}\left\{1-\frac{m^2}{(q+3)^2}\right\}\frac{c_{q+2}\,c_{q+3}}{[2q+2\,1]}, \tag{49}$$

$$\beta_0 = [212] + \frac{1}{9}\left(1-\frac{m^2}{4}\right)\frac{c_2{}^2}{[221]} + \frac{d_1{}^2[210]}{4[210][213]+m^2\,c_1{}^2}, \tag{50}$$

$$
\begin{aligned}
\beta_n = [2\ q+1\ 2] &+ \frac{1}{(2q+1)^2}\left\{1-\frac{m^2}{(q+1)^2}\right\}\frac{c_{q+1}^2}{[2\,q\,1]} + \frac{1}{(2q+3)^2}\left\{1-\frac{m^2}{(q+2)^2}\right\}\frac{c^2 q+2}{[2\,q+2\,1]}\\
&+ \frac{d_{q+1}^2\,[2\,q+1\,0]}{4\,[2\,q+1\,0][2\,q+1\,3]+m^2\,c_{q+1}^2} \qquad (n \geqq 1),
\end{aligned}
\tag{51}
$$

$$\gamma_n = \frac{c_q\,c_{q+1}}{[2\,q\,1]}, \qquad f = \frac{c_1\,d_1[210]}{4[210][213]+m^2\,c_1{}^2}\,\mathscr{B}^{210}. \tag{52, 53}$$

The set (47) is an inhomogeneous set of infinite coupled equations having ∞^1 solutions. Among these, a privileged solution will be found by successive approximations. The coefficients α_n are proportional to E^2 and in the low-field case can be assumed to be small. The n-th approximation will consist in taking into account $\alpha_0, \alpha_1, \ldots, \alpha_{n-1}$ and neglecting α_s for $s \geqq n$. The same solution is found if also the γ's (which are also proportional to E^2) are treated in the same manner as the α's. This method is certainly valid at low fields, but can be extended by continuity to high fields. All the other solutions, differing from the one described above by solutions of the associate homogeneous set, have pathological properties (at low fields ξ_n is strongly divergent for large n) and will be discarded as non-physical.

The physical solution is

$$\xi_0 = i\,m\,f\,R/\beta_0, \tag{54}$$

$$R = \lim_{n\to\infty}\left(D^{(1,n)}/D^{(0,n)}\right) \tag{55}$$

where, letting

$$p_n = -\,\alpha_n\,\gamma_{n+1}/\beta_n\,\beta_{n+1}, \tag{56}$$

$D^{(m,n)}$ is the determinant

$$
D^{(m,n)} \tag{57}
$$

$$
= \begin{vmatrix}
1 & 1 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0\\
-p_m & 1 & 1 & 0 & 0 & 0 & \ldots & 0 & 0 & 0\\
0 & -p_{m+1} & 1 & 1 & 0 & 0 & \ldots & 0 & 0 & 0\\
0 & 0 & -p_{m+2} & 1 & 1 & 0 & \ldots & 0 & 0 & 0\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
0 & 0 & 0 & 0 & 0 & 0 & \ldots & -p_{n-1} & 1 & 1\\
0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & -p_n & 1
\end{vmatrix}
$$

obeying the recursion relation

$$D^{(m,n)} = D^{(m,n-1)} + p_n\,D^{(m,n-2)} \tag{58}$$

and the initial conditions

$$D^{(m,m-1)} = 1, \qquad D^{(m,m)} = 1 + p_m. \tag{59}$$

The collision brackets contained in α_n, β_n, γ_n and f have been evaluated in the mean collision frequency approximation as follows:

$$[2\ q+1\ 0] = -\frac{1}{2}\,\frac{n\,\omega_c}{2q+3}\,\langle \nu_{q+1}(J^2)\rangle,$$

$$[\,2\;p\;1] = -\frac{1}{2}\,\frac{n\,\omega_c}{2q+1}\,\langle \nu_q(J^2)\rangle\,, \tag{60}$$

$$[2\;q+1\;2] = [2\;q+1\;3] = -\frac{1}{2}\,\frac{n\,\omega_c}{2q+3} \cdot \langle J_\zeta{}^2\,\nu_{q+1}(J^2)\rangle$$

where $\nu_q(J^2)$ is given by (37) and the collision frequency ω_c relevant for the phenomenon has been extracted from the experimental data of Korving for the viscosity of ammonia in a magnetic field[2].

The moments of inertia involved in the thermal averages contained in (35), (36) and (60) have been taken from Ref. [13].

The limit (55) has been computed numerically on a CAE 10070 computer by using Eqs. (58) and (59).

The convergence of the method is fast for all cases considered, both for NH_3 and for ND_3. Once $\xi_0 = \xi^{212m}$ has been obtained, ξ^{210m} can be derived easily with the result

$$\xi^{2101} = \xi^{210-1} = -\mathscr{B}^{210}\,\frac{c_1{}^2}{4[210][213]+c_1{}^2}\left\{1-\frac{d_1{}^2\,[210]}{4[210][213]+c_1{}^2}\;\frac{R}{[212]+\dfrac{1}{12}\,\dfrac{c_2{}^2}{[221]}+\dfrac{d_1{}^2[210]}{4[210][213]+c_1{}^2}}\right\} = -\mathscr{B}^{210}\,f(E) \tag{61}$$

$$\xi^{2100} = 0$$

whence, using (45), $\mathfrak{B}^{210}$ is obtained:

$$\mathfrak{B}^{210} = -\mathscr{B}^{210}\,f(E)\,(\tilde{\mathbf{S}}^{(2)} - \boldsymbol{e}\,\boldsymbol{e}\cdot\tilde{\mathbf{S}}^{(2)})\,. \tag{62}$$

Next the first equation of the set (34) is considered. $\mathfrak{B}^{200}$ is given by

$$\mathfrak{B}^{200} = -\frac{\begin{bmatrix}200\\210\end{bmatrix}}{200}\,\mathbf{S}\cdot{}^3\mathfrak{B}^{210} \tag{63}$$

and the relative change of the viscosity tensor equals $(\mathscr{B}^{200})^{-1}\,\mathfrak{B}^{200}$.

The tensorial properties and the saturation values of this change are exactly the same as in the magnetic case[14], except of course for the fact that the transverse components η_4 and η_5 vanish. The changes of the longitudinal components are

$$\Delta\eta_1 = 6\,\eta_0\,K,\quad \Delta\eta_2 = 4\,\eta_0\,K\,,\quad \Delta\eta_3 = 5\,\eta_0\,K \tag{64}$$

where

$$K = \frac{\begin{bmatrix}200\\210\end{bmatrix}}{[200][210]}\,f(E)\,. \tag{65}$$

$f(E)$ is rather complicated but at low pressures is approximately a function of E^2/p (quadratic for small values of E); at high pressures $f(E)$ becomes a function of E/p as is the case for the ordinary symmetric top molecules. The low pressure case is more interesting because Tommasini's measurements[3] have been performed in this range, and for this case $f(E)$ is reported in Figs. 3, 4 as a function of E^2/p. Fig. 5 shows the gradual change from the low to the high pressure behaviour.

Turning now to the anisotropic term $[\boldsymbol{J}]^{(2)}$ and the terms generated from it occurring in (23), a completely similar calculation can be performed. In this case the analogue of Eq. (25) is:

$$B = [\boldsymbol{W}]^{(2)}\cdot{}^2\mathbf{B}^{200} + \sum_{\substack{q=0\\ i=0,2,3}}^{\infty}{}'\,\alpha_i\,[\boldsymbol{J}]^{(2q)}\cdot{}^{2q}\mathbf{B}^{0,\,2q,\,i} + \sum_{q=0}^{\infty}\alpha_1\,[\boldsymbol{J}]^{(2q+1)}\cdot{}^{2q+1}\mathbf{B}^{0,\,2q+1,\,1}\,. \tag{66}$$

Following the previous method, a tensorial system analogous to (34) may be written; from this a set of numerical equations similar to (46) is obtained letting in place of (45):

$$\begin{aligned}
\mathbf{B}^{0\,q\,i} &= \sum_{-2^m}^{2}\xi^{0\,i\,m}\,\mathscr{P}(q,m)\,b^{q-2}\,\mathbf{E}^{(2)}\,, && (i=0,2,3;\; q>0;\; \text{not } i=0,\; q=2)\\
\mathbf{B}^{0\;q+1\;1} &= \sum_{-2^m}^{2}\xi^{0,\,q+1,\,1,\,m}\,\mathscr{P}(q+1,m)\,b^{q-1}\,\mathbf{E}^{(2)}\,, && (q>0) \qquad (67)\\
\mathbf{B}^{00\,i} &= \xi^{00i0}\,a^2\,\mathbf{E}^{(2)} = \xi^{00i0}\,[\boldsymbol{e}]^{(2)}\,, && (i=2,3)\\
\mathbf{B}^{011} &= \sum_{-1^m}^{1}\xi^{011m}\,\mathscr{P}(1,m)\,a\,\mathbf{E}^{(2)}\,, && \mathfrak{B}^{020} = \sum_{-2^m}^{2}\xi^{020m}\,\mathscr{P}(2,m)\,\mathbf{E}^{(2)}\,.
\end{aligned}$$

---

[13] Landolt-Börnstein, Zahlenwerte und Funktionen, I. Band, 2. Teil, p. 339, Springer-Verlag, Berlin 1951.

[14] A. C. Levi and F. R. McCourt, Physica **38**, 415 [1968].

In the present case, the diagonal collision brackets of rank q have the tensorial properties of $\mathbf{E}^{(q)}$ (this is an exact result, without any need of a spherical approximation). The contribution of this term to the change in the viscosity components is as follows:

$$\Delta\eta_1 = 0\,, \qquad \Delta\eta_2 = -\tfrac{1}{2}\,\eta_0 K_2\,, \qquad \Delta\eta_3 = -\,\eta_0 K_1 \tag{68}$$

where

$$K_m = \frac{\begin{bmatrix}200\\020\end{bmatrix}}{[200][020]}\, f_m(E) \tag{69}$$

$$f_m(E) = \frac{m^2 c_2^2}{[020][023] + m^2 c_2^2} \cdot \left\{ 1 - \frac{d_2^2\,[020]}{[020][023] + m^2 c_2^2}\; \frac{R_m}{[022] + \dfrac{1}{3}\dfrac{c_2^2}{[011]}\,\delta_{1m} + \dfrac{4}{25}\left(1 - \dfrac{m^2}{9}\right)\dfrac{c_3^2}{[031]}\,\dfrac{d_2^2\,[020]}{[020][023] + m^2 c_2^2}} \right\} \tag{70}$$

and R_m is the limit of a rate of determinants completely analogous to (55). The contribution (68) is negative. According to Korving this contribution decreases the effect on η_3 given in (64) by $20\,^0\!/_0$ [2]. The function $f_1(E)$ closely resembles $f(E)$, provided the same collision frequency is assumed in both cases, as shown in Fig. 6 (actually the collision frequency connected to $[\boldsymbol{J}]^{(2)}$ is a reorientation frequency which may differ considerably from that connected to $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$).

V. Comparison with the Experiments and Discussion

It is useful for the discussion to introduce the important concept of the inversion pressure p_i, defined as that pressure where the frequency of the collisions relevant for the problem equals ω_i, the inversion angular frequency. In the case of the viscosity SB effect $p_i = 4019$ torr (about 5 atm) for NH_3 and $p_i = 293$ torr for ND_3, if the data of Korving[2] are used for NH_3 and the relevant mean cross section is assumed to be the same for the heavy species. In the following, "low" and "high" pressures will always mean low and high compared to the inversion pressure.

In Figs. 3 and 4 the theory is compared with the experimental results obtained by Tommasini[3]. The agreement is reasonably good for both NH_3 and ND_3, except for the slope which is steeper for the theoretical curve. The latter defect is easy to

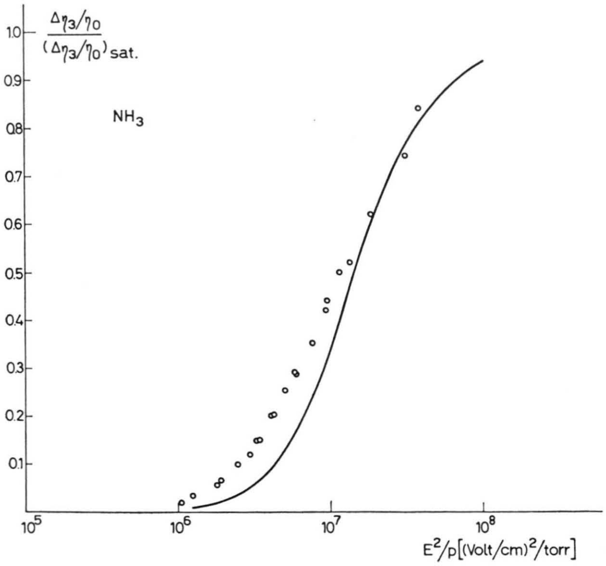

Fig. 3. Field dependence of the viscosity change for NH_3. Full line: theory; points: experimental data obtained by Tommasini[3].

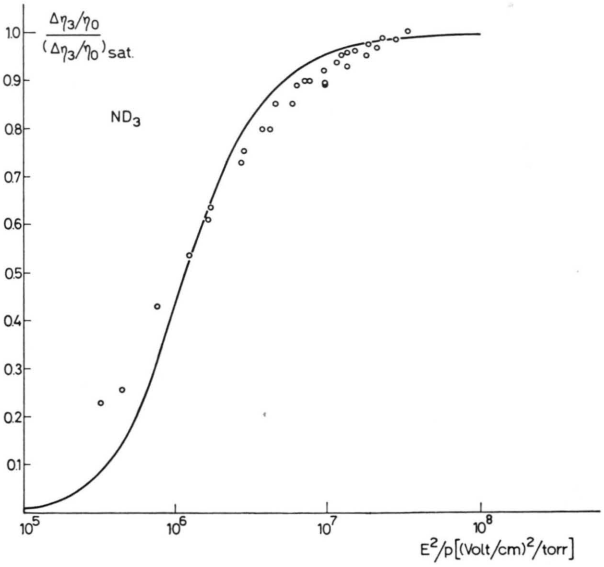

Fig. 4. Field dependence of the viscosity change at low pressures ($p < 5$ torr) for ND_3. Full line: theory; points: experimental data obtained by Tommasini[3].

explain: as has been discussed elesewhere[4] a full variational calculation should contain a complete set of orthogonal polynomials in the scalars J^2 and $J_\zeta{}^2$, in which case, in the mean collision frequency approximation, it turns out to be equivalent for the ordinary symmetric tops to a perturbative calculation. A somewhat rougher variational calculation, without any polynomial expansion, such as has been used in the present work or in Ref. [11], always gives rise to too steep field dependences because a mean precession frequency is used in place of a precession frequency distribution.

At low pressures all the theoretical points fall on one and the same curve as a function of E^2/p, in agreement with the experiments. In other words $E_{1/2}$, the field at which the effect is half-way to saturation, is proportional to $\sqrt{p}$ at low p. At high pressures the situation changes and $E_{1/2}$ becomes linear in p. In Fig. 5 $E_{1/2}/\sqrt{p}$ is plotted vs. p for heavy ammonia showing the gradual change from the low to the high pressure regime. Thus:

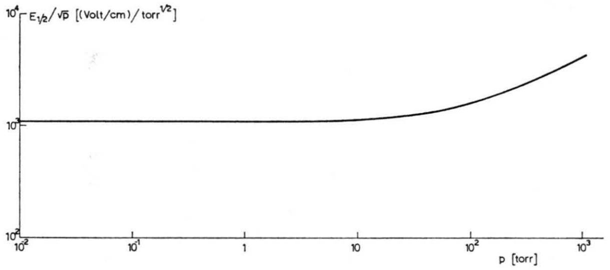

Fig. 5. Field at half-value of the effect divided by $\sqrt{p}$, vs. pressure [compare Eq.'s (71) and (72)] for ND_3.

$$\text{at low } p: \quad E_{1/2} \sim A\sqrt{p}, \quad A = 1080 \frac{\text{V}}{\text{cm} \cdot \text{torr}^{1/2}} \tag{71}$$

$$\text{at high } p: \quad E_{1/2} \sim Bp + E_0, \; B = 126 \frac{\text{V}}{\text{cm} \cdot \text{torr}}, \quad E_0 = 1570 \frac{\text{V}}{\text{cm}}. \tag{72}$$

E_0 is a positive field which may be interpreted as the field necessary to polarize the molecules in such a way that the eigenstates of the internal Hamiltonian become similar to $|\text{up}\rangle$ and $|\text{down}\rangle$, rather than $|+\rangle$ and $|-\rangle$. If the field is high enough there is little difference between heavy ammonia and any ordinary polar gas of symmetric top molecules. For light ammonia similar phenomena take place at higher pressures (and fields).

The mathematical methods used in the present work to treat the problems where the field couples tensors of different ranks in $\boldsymbol{J}$ could be extended to other cases, for example to linear molecules where such coupling, incorrectly neglected in Ref. [11], has been studied by HESS and MCCOURT[15] in the low-field range.

Finally, the problems concerning the sign and the saturation value of the effect will be briefly considered. The questions arising in this connection are: Why is the effect positive for ammonia and only for ammonia? Is really the term $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ dominant and if so why? And so on. No definite answer can be given to such questions at the present moment, but a few comments are in order.

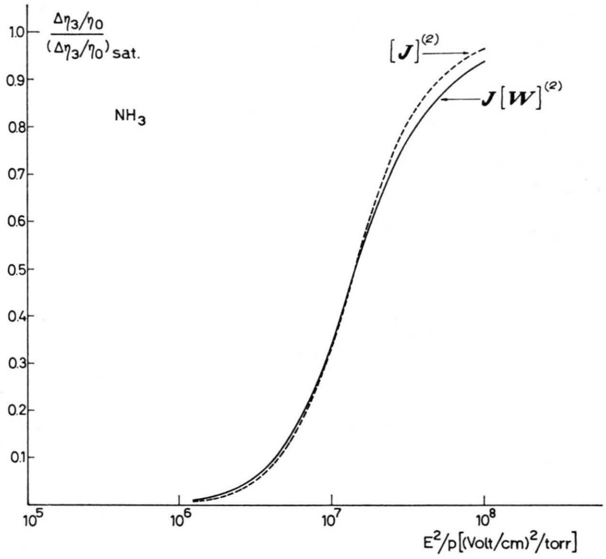

Fig. 6. Comparison between the field dependences of the change in η_3 from $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ (full line) and $[\boldsymbol{J}]^{(2)}$ (dashed line).

First of all, the collision bracket $\left[{}^{200}_{020}\right]$ appears to be exceptionally small in the case of ammonia[2]. This collision bracket is related to energetically inelastic collisions and vanishes in the absence of such collisions[16]. Now ammonia, because of its high hydrogen content, has very small moments of inertia, so that the rotational energy levels are widely separated. As a consequence, the collision process is nearly adiabatic: the duration of a

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collision is rather long in comparison to $\hbar/\Delta E$, and the transition probability is small. Moreover, transitions involving a change of K are restricted by selection rules prohibiting conversion of A-ammonia into E-ammonia or viceversa. Hence energetically inelastic collisions should indeed be exceptionally rare in ammonia. This implies a drastic reduction of the contribution from the term $[\boldsymbol{J}]^{(2)}$, and correspondingly a dominance of other terms. Korving's analysis[2] indicates a strong dominance of $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$. This is not very surprising, since $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ is the next simplest term in the expansion and since the dipole-dipole interaction, very far from being spherical, causes certainly many collisions without an inverse to occur, thereby allowing large contributions from the terms odd in $\boldsymbol{J}$[14]. In the authors' opinion the positive sign of the effect should not be related to the inversion of the molecule, the latter effect being much too slow to affect the collisions. Indeed, if inversion was important, the effect should be qualitatively different in heavy ammonia where inversion is 15 times slower, in contradiction to experiments.

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The Slip Problems for a Simple Gas

S. K. LOYALKA *

Max-Planck-Institut für Strömungsforschung, Göttingen, Germany

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Simple and accurate expressions for the velocity slip coefficient, the slip in the thermal creep, and the temperature jump coefficient are obtained by applying a variational technique to the linearized Boltzmann equation for a simple gas. Completely general forms of the boundary conditions are used, and the final results are presented in a form such that the results for any particular intermolecular force law or the gas-surface interaction law can easily be calculated. Further, it is shown that, with little extra effort, the present results can be easily extended to include the case of a polyatomic gas. It is felt that the present work, together with a recent paper in which the author has considered the solutions of the linearized Boltzmann equation for a monatomic multicomponent gas mixture, provide the desired basis for the consideration of the various slip problems associated with the polyatomic gas mixtures.

I. Introduction

Recently, in a series of papers we[1–4] have considered the slip problems for a simple monatomic gas. In these studies, we applied variational techniques (for some general remarks on the use of the variational techniques in the kinetic theory, see Refs. [4, 5]) to the linearized Boltzmann equation and we were able to obtain some simple and very accurate results. However, in this work, for the gas-wall interaction, we considered either the diffuse reflection[1, 2, 4], or the Maxwell's diffuse-specular reflection[3]. Since some recent molecular beam experiments[6, 7] have indicated that the above forms of the gas-wall interaction, are, in fact, very severe approximations of the actual forms of the gas-wall interaction, an extension of our work to include more general cases may be of considerable interest.

Reprints request to Dr. S. K. LOYALKA, Max-Planck-Institut für Strömungsforschung, *D-3400 Göttingen*, Böttingerstraße 6/8.

* On leave, Academic years 1969—71, from the Department of Nuclear Engineering, University of Missouri-Columbia, Missouri 65 202, USA.

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