[33] In this case (5) reduces to $\rho_3(x_1x_2\vec{R}, x'_1x'_2\vec{R}') = f_0(x_1x_2\vec{R}) \times f_0^*(x'_1x'_2\vec{R}')$, and the desired result follows immediately from (26) upon noting that f_0 is translationally invariant and normalized.

[34] In fact it is easy to show, in analogy with the derivation of (82), that if one replaces (38) by an unsymmetrized product $g(x_1x_2)g(x_3x_4)\cdots g(x_{2n-1}x_{2n})$, then (21) implies $f_{\vec{k}} = n\delta_{\vec{k}0}$ if g is any normalized and translationally invariant two-electron state. However, this result is incompatible with the exclusion principle.

[35] We assume, without essential loss of generality, that $g_{\vec{k}}$ is real and an even function of $\vec{k}$.

[36] See, e.g., M. Girardeau and R. Arnowitt, Phys. Rev. 113, 755 (1959).

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Influence of a Magnetic Field on the Transport Coefficients of Oxygen Gas: Anomalies Associated with the $\sigma = 0$ Multiplets[*]

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The transport coefficients of $^3\Sigma$ molecular oxygen in magnetic fields show large deviations from an H/p law, even at moderate pressures and fields. This complex behavior is explained by the effect of a quadratic Zeeman splitting of the $\sigma = 0$ multiplets, superimposed on the normal linear splitting. Because the normal linear splitting is very small for $\sigma = 0$, the anomalous effects occur at fields far below the true Paschen-Back region. Collisionally uncoupled model calculations give the transverse viscosity coefficients in quite detailed agreement with experiment. The distinct behavior of the single- and double-frequency viscosity coefficients reflects distinct selections from the internal-state frequency spectrum, determined by weight factors $|Y^{2\mu}(\theta, \phi)|^2$ in the orientation of $\vec{J}$. The anomalous behavior of the even coefficients is predicted to be quite complex. In particular the H/p curves of η_1^+ at about 4 Torr should show three steps, instead of the usual two, and the behavior of $\lambda_\parallel$ should be similar.

I. INTRODUCTION

The effect of a magnetic field on the thermal conductivity and viscosity of dilute gases is commonly a function of the ratio H/p of the field strength to the pressure. According to the picture of Gorter,[1] the explanation of this H/p dependence is that the effects are functions of the product $\omega\tau$ of a precession frequency, proportional to the field, and a relaxation time, of the order of the time between collisions and proportional to $1/p$. Kikoin *et al.*,[2] however, found very large deviations from H/p behavior for one of the transverse viscosity coefficients of $^3\Sigma$ oxygen. Recent very precise measurements of Hulsman *et al.*[3] not only confirm Kikoin's result, but show that the other transverse coefficient is also anomalous, and furthermore that the behavior of the two coefficients is quite distinct. In both H/p plots the shoulder which occurs at lower H/p behaves normally at constant pressures up to one atmosphere. This feature is associated[4,5] with molecules in states belonging to multiplets having total angular momentum $J = N \pm 1$, where N is the [Hund's case (b)] rotational quantum number. Alternatively, these multiplets may be labeled by $\sigma = \pm 1$, where $\sigma = J - N$ is the spin projection on $\vec{J}$ in the classical (large N) limit. The peak occurring at higher H/p however, and which is associated with multiplets having $\sigma = 0$ $(J = N)$, disappears with increasing pressure. Significant cutting off on the high-field side of this peak occurs at pressures of only a few Torr, and one of the viscosity coefficients, but not the other, changes sign.

Deviations from H/p behavior can likewise be seen in the even thermal-conductivity and viscosity coefficients measured by Kikoin *et al.*,[2] Korving *et al.*,[6] and Hermans *et al.*[7] at room temperature, and indeed—though for higher pressures—in the early measurements of Senftleben and Piezner[8] (see Hermans[7] for a comparison). The very pronounced scatter of the points near saturation is shown clearly in Korving's[6] H/p plots on "probability" paper.

It is the object of this paper to give an explanation of this behavior. The quantitative theory is given for the viscosity only, but the qualitative picture applies, with minor modifications, to the thermal conductivity also.

II. VISCOSITY THEORY FOR SMALL DEVIATIONS FROM LOW-FIELD STATES

Deviations from H/p behavior in the paramagnetic Senftleben effects usually reflect the mixing by the field of states belonging to different zero-field multiplets (the Paschen-Back effect), and in particular the associated deviations from a linear Zeemann energy-level splitting.[9,10] The deviations from H/p behavior increase with increasing pressure because the normal H/p relation means that higher pressures imply higher fields. It will be shown that the explanation of the oxygen anomalies is the mixing of the $\sigma = 0$ states with the $\sigma = \pm 1$ states having the same rotational quantum number N, even though the fields involved are relatively low.

The effect of level splittings nonlinear in the field can be taken into account very simply in a collisionally uncoupled model. Nonlinear splittings imply that the spacing between energy levels is not constant. Hence the single Larmor frequency for the multiplet is broadened into a spectrum of frequencies. According to collisionally uncoupled theory, each frequency $\omega(H)$ is associated with an independent contribution to the transport coefficients, characterized by a separate product $\omega\tau$. The transport coefficients are suitably weighted superpositions of these contributions. For a detailed formal development see Ref. 5.

In oxygen, the eigenstates of the free-molecule Hamiltonian, including the effect of the field, can be labeled $|N\sigma m\rangle$ in the Hund's case (b) approximation. Formally,[5] each internal-state polarization $|N\sigma m\rangle\langle N\sigma m'|$ makes an independent contribution to the viscosity characterized by the frequency $\omega^{N\sigma}_{m,m'} = (E_{N\sigma m} - E_{N\sigma m'})/\hbar$ of its harmonic motion between collisions, and by an orientational relaxation time $\tau_{N\sigma}$ which depends on the multiplet, but which is assumed not to depend on m and m'. For a uniform magnetic field along the z axis, m and m' label the eigenvalues of $J_z = N_z + S_z$ (which is well defined in the energy states even in strong fields). If correlated velocity–angular-momentum polarizations of the type $[\vec{\mathrm{W}}]^{(t)}|N\sigma m\rangle\langle N\sigma m'|$ (cf. $[\vec{\mathrm{W}}]^{(2)}[\vec{\mathrm{J}}]^{(2)}$) are neglected, where $\vec{\mathrm{W}}$ denotes the reduced peculiar velocity and $[\vec{\mathrm{W}}]^{(j)}$ an irreducible tensor of rotational symmetry j constructed from $\vec{\mathrm{W}}$, then the polarizations contributing to the nonvanishing even and odd elements η^{+}_{μ} and η^{-}_{μ} of the real spherical viscosity tensor, appropriate to this case,[5] obey the selection rule

$$\Delta m = m' - m = \mu \ . \tag{1}$$

The viscosity coefficients $\eta^{\pm}_{\mu}$ relate the real spherical components of the symmetry-2 (traceless symmetric) parts of the pressure and velocity gradient tensors by

$$\Pi^{(2)\mu\pm} = -2\{\eta^{+}_{\mu}[\vec{\nabla}\vec{\mathrm{v}}_0]^{(2)\mu\pm} \mp \eta^{-}_{\mu}[\vec{\nabla}\vec{\mathrm{v}}_0]^{(2)\mu\mp}\} , \tag{2a}$$

and, apart from notation, differ in only two respects from the five nontensorial parameters of Hooyman, Mazur, and DeGroot,[11] in terms of which considerable experimental data has been reported (see Table I). Explicitly, Eq. (2) is

$$\begin{pmatrix} (\frac{3}{2})^{1/2}\Pi^{(2)}_{zz} \\ \Pi_{xz} \\ \Pi_{yz} \\ \frac{1}{2}(\Pi_{xx} - \Pi_{yy}) \\ \Pi_{xy} \end{pmatrix} = -2 \begin{pmatrix} \eta^{+}_{0} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \eta^{+}_{1} & -\eta^{-}_{1} & \cdot & \cdot \\ \cdot & \eta^{-}_{1} & \eta^{+}_{1} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \eta^{+}_{2} & -\eta^{-}_{2} \\ \cdot & \cdot & \cdot & \eta^{-}_{2} & \eta^{+}_{2} \end{pmatrix} \begin{pmatrix} (\frac{3}{2})^{1/2}\mathbf{S}_{zz} \\ \mathbf{S}_{xz} \\ \mathbf{S}_{yz} \\ \frac{1}{2}(\mathbf{S}_{xx} - \mathbf{S}_{yy}) \\ \mathbf{S}_{xy} \end{pmatrix} , \tag{2b}$$

where $\mathbf{S}_{rs}$ has been written for

$$[\vec{\nabla}\vec{\mathrm{v}}_0]^{(2)}_{rs} = \frac{1}{2}\left(\frac{\partial v_{0r}}{\partial x_s} + \frac{\partial v_{0s}}{\partial x_r}\right) - \frac{1}{3}(\vec{\nabla}\cdot\vec{\mathrm{v}}_0)\delta_{rs} ,$$

and where the dots indicate those tensor elements which vanish because of the axial symmetry.

For the relatively low fields of interest here, and with correlated polarizations neglected, the expression given by the uncoupled model for the relative contributions of the orientational polarizations to the viscosity coefficients is

$$\frac{\overline{\Delta\eta^{\pm}_{\mu}}}{\overline{\eta}} = \sum_{N,\sigma} b_N \mathscr{I}_{N\sigma}\Bigg((2J+1)^{-1} \times \sum_{m} |\langle J, m+\mu|\mathbf{Y}^{2\mu}(\vec{\mathrm{J}})|J, m\rangle|^2 f^{\pm}(\omega^{N\sigma}_{m+\mu,m}\tau_{N\sigma})\Bigg) . \tag{3}$$

where $J = N + \sigma$. Here $\overline{\eta}$ is the scalar viscosity coefficient in the absence of orientational polarizations, b_N is the Boltzmann probability factor for the multiplet $\{N, \sigma\}$, which can be taken as $Q^{-1}e^{-B\vec{N}^2/kT}$, independent of σ, $\mathscr{I}_{N\sigma}$ is an intensity factor for the whole multiplet, while the purely geometric intensity factors $|\langle J, m+\mu|\mathbf{Y}^{2\mu}(\vec{\mathrm{J}})|J, m\rangle|^2$ give the relative weighting of the contributions associated with the different frequencies within the multiplet. The symmetry-2 tensor operator $\mathbf{Y}^{(2)}(\vec{\mathrm{J}})$ is the quantum analog of the purely angular spherical harmonic $Y^{2\mu}(\theta, \phi)$ in the orientation of $\vec{\mathrm{J}}$. It is defined in terms of the corresponding *solid* harmonic $[\vec{\mathrm{J}}]^{(2)}$, having Cartesian components $[\vec{\mathrm{J}}]^{(2)}_{rs} = \frac{1}{2}(J_rJ_s + J_sJ_r) - \frac{1}{3}\vec{\mathrm{J}}^2\delta_{rs}$, by

$$\mathbf{Y}^2(\vec{\mathrm{J}}) = (\sqrt{5})\textstyle\sum_J\{\frac{2}{3}\vec{\mathrm{J}}^2(\vec{\mathrm{J}}^2 - \frac{3}{4})\}^{-1/2}[\vec{\mathrm{J}}]^{(2)}\mathcal{P}_J , \tag{4}$$

where $\mathcal{P}_J$ is a projection onto the space of angular momentum states having quantum number J. The normalized tensor $\mathbf{Y}^2(\vec{J})$ is essentially independent of the magnitude of $\vec{J}$, and describes purely angular polarizations. The functions f^+ and f^- are Lorentz absorption and dispersion shape functions, namely,

$$\begin{aligned} f^+(x) &= (1+x^2)^{-1} , \\ f^-(x) &= x(1+x^2)^{-1} . \end{aligned} \tag{5}$$

Explicitly, the multiplet intensity factor is given by

$$\mathcal{g}_{N\sigma} = (2J+1)\varphi^2_{N\sigma}\tau_{N\sigma}/R_W . \tag{6}$$

Here $\varphi_{N\sigma}$ is a scalar collision integral which gives the coupling between the velocity polarization $[\vec{W}]^{(2)}$ and the angular momentum $\mathbf{Y}^2(\vec{J})$ polarization associated with molecules in states belonging to the $\{N, \sigma\}$ multiplet (i.e., $\mathbf{Y}^2(\vec{J})\mathrm{P}_{N\sigma}$). It is defined by

$$\varphi_{N\sigma} = (2J+1)^{-1}\mathrm{tr}_m \int \tfrac{1}{5} f_W^{(0)} \mathbf{Y}^2(\vec{J}) : (\mathcal{R}[\vec{W}]^{(2)})\, d\vec{p} , \tag{7}$$

where $f_W^{(0)} = (2\pi mkT)^{-3/2} e^{-W^2}$ is the local equilibrium velocity distribution, and $\mathcal{R}$ the collision operator. The trace is only over the $(2J+1)$ substates of the $\{N, \sigma\}$ multiplet. The normalization is such that $\varphi_{N\sigma}$ can reasonably be assumed to be multiplet independent,[5] so that $\varphi_{N\sigma} = \varphi$ for all $\{N, \sigma\}$. For the present considerations φ can be regarded as an unknown constant. The quantity R_W is the scalar collision integral defined by

$$R_W = (n^{-1}/5)\,\mathrm{tr} \int f^{(0)}[\vec{W}]^{(2)} : (R[\vec{W}]^{(2)})\, d\vec{p} , \tag{8}$$

where $f^{(0)}$ includes the equilibrium internal-state density matrix as well as $f_W^{(0)}$ and where the trace is over all internal states, unlike the trace in Eq. (7). This integral determines the scalar viscosity coefficient $\overline{\eta}$ when the contribution of internal-state polarizations is neglected, in which case $\eta_\mu^+ = \overline{\eta} = \frac{1}{2}nkTR_W^{-1}$ and $\eta_\mu^- = 0$ (all μ).

It should be noted that $\overline{\Delta}\eta_\mu^\pm$ given by expression (3) is the actual *contribution* of the internal-state polarizations to $\eta_\mu^\pm$ (to second order in the velocity–internal-state coupling), and not the *change* $\Delta_{\mathrm{field}}(\eta_\mu^\pm) = \eta_\mu^\pm(H) - \eta_\mu^\pm(0)$ in the viscosity produced by the external field. The latter is the quantity measured experimentally. For the odd coefficients there is in fact no distinction since η_μ^- vanishes at zero field. However, for the even coefficients the relation is

$$\Delta_{\mathrm{field}}(\eta_\mu^+) = \overline{\Delta}\eta_\mu^+(H) - \overline{\Delta}\eta_\mu^+(0) , \tag{9}$$

and this is given by Eq. (3) on replacing f^+ by

$$f^+_{\mathrm{field}}(x) = f^+(x) - 1 = -x^2(1+x^2)^{-1} . \tag{10}$$

The point is that the field destroys the contribution of internal polarizations to the even viscosity coefficients.

The $\sigma = 0$ and $\sigma = \pm 1$ contributions may be considered separately. For the $\sigma = \pm 1$ multiplets there is no significant deviation from the linear Zeemann effect over most of the region of field strengths considered. Consequently, for given μ, there is only a single frequency $\omega^{N\sigma}_{m,m-\mu} = \mu\omega_{N\sigma}$ for each multiplet, where $\omega_{N\sigma}$ is the multiplet Larmor frequency. The $\sigma = \pm 1$ terms in Eq. (3) then reduce to

$$\left(\frac{\overline{\Delta}\eta_\mu^\pm}{\overline{\eta}}\right)^{\cdot}_{\sigma=\pm 1} = \sum_{N,\sigma=\pm 1} b_N \mathcal{g}_{N\sigma} f^\pm(\mu\omega_{N\sigma}\tau_{N\sigma}) . \tag{11}$$

This expression accounts for the low field $\sigma = \pm 1$ feature satisfactorily.

For $\sigma = 0$, on the contrary, the existence of a spectrum of frequencies within each multiplet must be taken into account. The weight factors $|\langle J, m+\mu | \mathbf{Y}^{2\mu}(\vec{J}) | J, m\rangle|^2 = |\mathrm{tr}\{(|J, m\rangle\langle J, m+\mu|) \times \mathbf{Y}^{2\mu}(\vec{J})|^2$ represent, loosely, the square of the probability distribution of J and m associated with the polarization $\mathbf{Y}^{2\mu}(\vec{J})$. For large J, corresponding to the fact that $\mathbf{Y}^{2\mu}(\vec{J})$ represents angular polarization, this probability distribution is a function only of the orientation of $\vec{J}$ with respect to the field, as defined by

$$\cos\theta = m/(\vec{J}^2)^{1/2} . \tag{12}$$

In fact $\langle J, m+\mu | \mathbf{Y}^{2\mu}(\vec{J}) | J, m\rangle \to 2^{1/2}\tilde{p}_2^\mu(\cos\theta) = (4\pi)^{1/2} | Y^{2\mu}(\theta\phi)|$ for $J \gg \mu$, where $\tilde{p}_2^\mu(\cos\theta)$ is the normalized associated Legendre function. In this large J approximation the frequencies can be written

$$\omega^{N\sigma}_{m+\mu,m} = \mu\omega_{N\sigma}(\theta) , \tag{13}$$

and, if θ is treated as a continuous variable, the $\sigma = 0$ contribution to $\overline{\Delta}\eta_\mu^\pm$ becomes

$$(\overline{\Delta}\eta_\mu^\pm/\overline{\eta})_{\sigma=0} = \textstyle\sum_N b_N \mathcal{g}_{N0}$$

$$\times \int_{-1}^{1} |\tilde{p}_2^\mu(\cos\theta)|^2 f^\pm(\mu\omega_{N0}(\theta)\tau_{N0})\, d\cos\theta , \tag{14}$$

where, in particular

$$\begin{aligned} \tilde{p}_2^1(\cos\theta) &= (\tfrac{15}{4})^{1/2}\sin\theta\cos\theta , \\ \tilde{p}_2^2(\cos\theta) &= (\tfrac{15}{16})^{1/2}\sin^2\theta . \end{aligned} \tag{15}$$

The weight factor $|\tilde{p}_2^\mu(\cos\theta)|^2$ can equally well be written $|Y^{2\mu}(\theta, \phi)|^2$, with integration over the whole orientation sphere of $\vec{J}$, emphasizing the corre-

TABLE I. Relation of the parameters of Hooyman, Mazur, and DeGroot (Ref. 11) to the real tensorial viscosity coefficients $\eta_\mu^\pm$.

μ	η_μ^+	η_μ^-
0	η_1	...
1	η_3	η_5
2	$2\eta_2 - \eta_1$	$-\eta_4$

spondence to the classical polarization tensor $[\vec{\mathrm{J}}]^{2\mu}_{\mathrm{classical}} = (\frac{8}{15}\pi)^{1/2} J^2 Y^{2\mu}(\theta, \phi)$. The partially classical expression (14) is useful in understanding the anomalous effects qualitatively, and it is sufficiently accurate for the calculation of the viscosity coefficients at room temperature.

III. FREQUENCY SPECTRUM

The first point to be understood in the oxygen effects is why the deviations from H/p behavior set in at very low fields. Anomalies are significant even at 300 Oe, whereas the critical Paschen-Back region of intermediate coupling, corresponding to the 2-cm^{-1} energy separation between the $\sigma = 0$ and $\sigma = \pm 1$ multiplets on an N shell, occurs in the region 20 000 Oe.

It may be enquired first whether high-field anomalies occurring at comparatively low fields could be associated with the mixing of the closely spaced $\sigma = +1$ and $\sigma = -1$ multiplets on the same N shell. However, since the field does not mix the $\sigma = \pm 1$ multiplets directly (cf. Appendix), the relevant spacing is not that between $\sigma = +1$ and $\sigma = -1$, but rather the much larger spacing between $\sigma = \pm 1$ and $\sigma = 0$. Furthermore, the $\sigma = \pm 1$ feature in the H/p curves occurs for a given pressure at fields lower by a factor of order N than the $\sigma = 0$ feature (~ 50 Oe for $p = 10$ Torr). It is therefore not expected that large anomalous effects at low fields can be associated with the $\sigma = \pm 1$ multiplets.

The explanation of the observed anomalies starts from the observation that the normal linear Zeemann level splitting is very small for $\sigma = 0$ because the spin $\vec{\mathrm{S}}$ is nearly perpendicular to $\vec{\mathrm{J}}$. The spin becomes increasingly perpendicular with increasing quantum number N, and the magnetic moment for the multiplet tends to zero as $1/N$. The Larmor frequency is therefore of order $\gamma_s \hbar H/\vec{\mathrm{N}}^2$, as compared to $\pm \gamma_s \hbar H/N$ for the $\sigma = \pm 1$ multiplets, a difference manifested by the occurrence of the $\sigma = 0$ feature at relatively high H/p. Because the normal linear Zeemann splitting is so small, it follows that even a small quadratic term can have a dramatic effect. This is why the Paschen-Back anomalies occur at such low fields.

When the quadratic term is included, the energy-level splittings are given by (see Appendix)

$$E_{N0m} = E_{N,0} - \frac{\gamma_s \hbar H}{\vec{\mathrm{N}}^2}\, m + \frac{(\gamma_s \hbar H)^2}{\lambda}\left[1 - \frac{m^2}{\vec{\mathrm{N}}^2}\left(1 + \frac{1}{\vec{\mathrm{N}}^2}\right)\right], \tag{16}$$

where λ is the spectroscopic spin-spin splitting parameter which gives the approximate zero-field separation between the $\sigma = 0$ multiplet and the $\sigma = \pm 1$ multiplets. For large N this formula may be written

$$E_{N,0}(\theta) = E_{N,0} - \frac{\gamma_s \hbar H}{|N|}\cos\theta + \frac{(\gamma_s \hbar H)^2}{\lambda}\sin^2\theta \ , \tag{17}$$

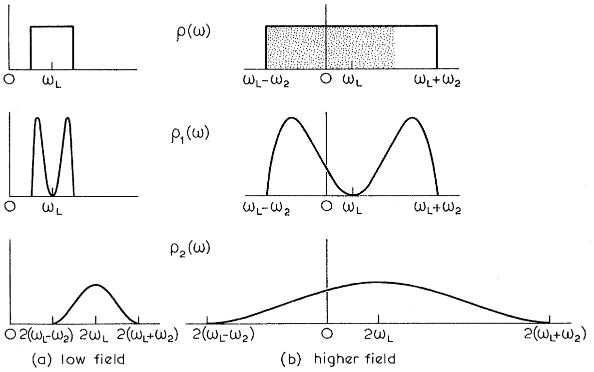

FIG. 1. The frequency density $\rho(\omega)$ and frequency weight factors $\rho_\mu(\omega)$ for $\mu = 1, 2$. Case (a): $\omega_2 = \frac{1}{2}\omega_L$ (for which all frequencies are positive); case (b): $\omega_2 = 3.33\omega_L$ (for which some frequencies are negative). The scales in (a) and (b) are not the same. The shaded area in $\rho(\omega)$ shows those positive and negative frequencies whose contributions to the transverse coefficients would exactly cancel in the absence of the weight factors $|\bar{p}_2^\mu(\cos\theta)|^2$.

where $|N| = (\vec{\mathrm{N}}^2)^{1/2}$. If θ is regarded as a continuous variable, then the $\Delta m = 1$ spectrum is given by

$$\omega_{N,0}(\theta) = |N|^{-1}[dE_{N,0}(\theta)/d\cos\theta] = \omega_L - \omega_2 \cos\theta \ , \tag{18}$$

where $\omega_L = \omega_L(N, H)$ is the normal $\sigma = 0$ multiplet Larmor frequency, while $\omega_2 = \omega_2(N, H)$ is the quadratic term

$$\omega_L = -\gamma_s \hbar H/N^2 \ , \quad \omega_2 = 2(\gamma_s \hbar H)^2/|N|\lambda \ . \tag{19}$$

Accordingly, the single Larmor frequency is broadened into a band of frequencies of uniform density

$$\rho(\omega_{N,0}) = \left|\frac{\partial\cos\theta}{\partial\omega_{N,0}}\right| = \omega_2^{-1} \ , \tag{20}$$

distributed equally about ω_L between $\omega_L - \omega_2$ and $\omega_L + \omega_2$. Figure 1 illustrates this.

The frequencies associated with orientations $\theta < \frac{1}{2}\pi$ eventually become negative with increasing field, and tend to cancel the contribution to the transverse effects of equal positive frequencies. This sign change is the origin of the disappearance of the $\sigma = 0$ peak at higher pressures. The change of sign of a $\Delta m = 1$ frequency corresponds to the crossing of two adjacent m levels. Such crossings occur as the low-field Zeemann pattern of energy levels changes to the quite different Stark pattern of the quadradic term. A level crossing at ~ 5000 Oe can be seen in a graph given by Tinkham and Strandberg[12] for $N = 3$. As the quadradic term is of order $1/N$, whereas ω_L is of order $1/N^2$, the level crossings, and the anomalous effects, set in at progressively lower fields with increasing N. One of the consequences is that the anomalies should be more important at higher than at lower temperatures. For orientations $\theta < \frac{1}{2}\pi$, the sign change in frequency occurs at a field H satisfying $-(\gamma_s \hbar H)\cos\theta = \lambda/2N \sim (1.0/N)\ \mathrm{cm}^{-1}$, that is for

$$H\cos\theta \sim 10\,000/N\ \mathrm{Oe}\ . \tag{21}$$

As the highest multiplets contributing significantly to the viscosity at room temperature are those with $N \sim 30$, the anomalies can set in at a few hundred oersted.

The mere disappearance of the transverse $\sigma = 0$ peaks can be predicted without any formal theory of the transport coefficients, simply because the Stark pattern corresponds to a Hamiltonian $\mathcal{H} = (\gamma_s^2/\lambda)(\vec{H}\cdot\vec{J})^2$ which has even σ_v symmetry, whereas η_μ^- is odd under σ_v. Since the phenomenological coefficients are necessarily totally symmetric under the symmetry group of the Hamiltonian, η_μ^- has to vanish.

The detailed effects depend on the selections of frequencies made by the weight factors $|\tilde{p}_2^\mu(\cos\theta)|^2$. To see the qualitative picture, it is convenient to rewrite these as functions of frequency, rather than of the orientation of $\vec{J}$. Define the frequency weight factors as

$$\rho_\mu(\omega_{N,0}) = |\tilde{p}_2^\mu(\cos\theta(\omega_{N,0}))|^2\, |d\cos\theta(\omega_{N,0})/d\omega_{N,0}|$$
$$= \omega_2^{-1} |\tilde{p}_2^\mu(\cos\theta(\omega_{N,0}))|^2\ . \tag{22}$$

Then, from Eq. (14), the contribution of a typical multiplet can be written

$$(\overline{\Delta}\eta_\mu^\pm)_{N,0}/b_N\overline{\eta} = \mathcal{G}_{N,0} \int_{\omega_L-\omega_2}^{\omega_L+\omega_2} \rho_\mu(\omega) f^{\pm}(\mu\omega\tau_{N,0})\, d\omega. \tag{23}$$

Figure 1 illustrates these frequency weight factors for $\mu = 1$ and $\mu = 2$. The fact that the weight factor ρ_1 is bimodal, and that the maximum for the negative frequencies is not in general cancelled by the maximum of the positive frequencies, accounts for the fact that $-\eta_1^-$ has an H/p curve which is positive at low H/p and negative at high H/p. The detailed anomalous behavior of all four field-dependent coefficients can best be understood from the following weight factors for the magnitudes of the frequencies:

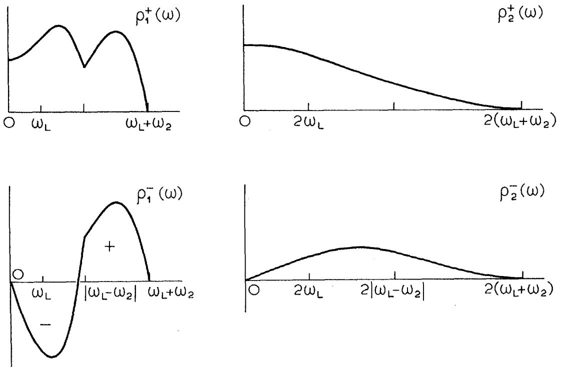

FIG. 2. Frequency weight factors $\rho_\mu^\pm(\omega)$ for the four field-dependent viscosity coefficients $\eta_\mu^\pm$, for the case $\omega_2 = 3.33\omega_L$ of Fig. 1(b).

$$\rho_\mu^\pm(|\omega|) = \rho_\mu(|\omega|) \pm \rho_\mu(-|\omega|)\ . \tag{24}$$

In these terms, expression (23) can be rewritten

$$\frac{(\overline{\Delta}\eta_\mu^\pm)_{N,0}}{b_N\overline{\eta}} = \mathcal{G}_{N,0} \int_0^{\omega_L+\omega_2(N)} \rho_\mu^\pm(\omega) f^{\pm}(\mu\omega\tau_{N,0})\, d\omega\ , \tag{25}$$

as an integral over positive frequencies only. Figure 2 shows the four weight functions for a field such that $\omega_2 = 3.33\omega_L$.

IV. VISCOSITY

It is argued elsewhere[5] that for diatomic molecules the relaxation time $\tau_{N\sigma}$ for reorientation should be proportional to $\vec{J}^2$. With this assumption, the relaxation time for the polarizations appropriate to the viscosity (as distinct from that for the thermal conductivity) may be written

$$\tau_{N\sigma} = \tau_0 \vec{J}^2/p\ , \tag{26}$$

where $J = N + \sigma$, and where τ_0 is multiplet and pressure independent. For numerical calculations, any small multiplet dependence of the normalized coupling terms $\varphi_{N\sigma}$ [Eq. (7)] will be neglected. Then the intensity factors are given by

$$\mathcal{G}_{N\sigma} = (2J+1)\vec{J}^2 I\ , \tag{27}$$

where I is a multiplet and pressure-independent constant. Apart from the over-all intensity factor I, the theory contains only the single unknown parameter τ_0. This has been chosen empirically as $2\pi\tau_0 = 0.30(10^{-8})$ Torr sec at room temperature, to fit the *position* of the $\sigma = 0$ peak in the experimental[3] H/p curves for η_2^- at low pressure. The remaining parameters are spectroscopic ($B/kT = \frac{1}{140}$, $-\gamma_s\hbar = 2.803$ MHz/Oe, $\lambda = 1.984\ \mathrm{cm}^{-1} = 5.948 \times 10^4$ MHz). Thus $\omega_L/2\pi = (2.8\times 10^6/\vec{N}^2)H\ \mathrm{sec}^{-1}$, while $\omega_2/2\pi = (2.6418 \times 10^2/|N|)H^2\ \mathrm{sec}^{-1}$, for H in oersted. The integrals in Eq. (14) can be evaluated analytically, but numerical integration is convenient.

Transverse Viscosity Coefficients

Figures 3(a) and 3(b) show the H/p curves for the $\sigma = 0$ contribution to the transverse viscosity coefficients, η_1^- and η_2^-, calculated from Eq. (14) together with Eqs. (18), (26), and (27) for the various constant pressures of Hulsman's[3] measurements, as well as for $p = 0$. The curves for $p = 0.1$ Torr differ negligibly from those for $p = 0$. The $p = 0$ envelope

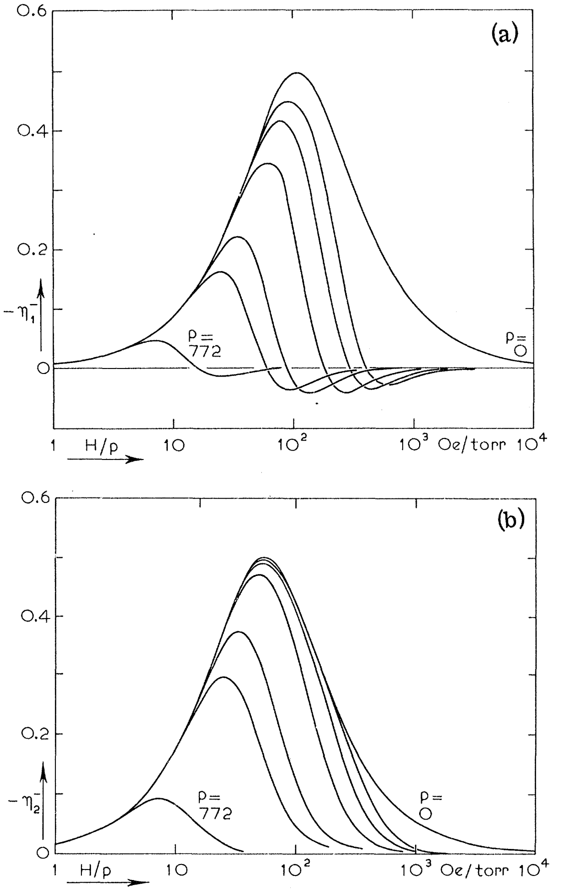

FIG. 3. (a) Calculated $\sigma = 0$ contribution to $-\eta_1^-$. Pressures from the right: 0.0, 4.1, 6.0, 10.9, 31.6, 61.3, and 772 Torr. (b) Calculated $\sigma = 0$ contribution to $-\eta_2^-$. Same pressures as in (a).

is a pure Lorentz curve because of the exact compensation between the N dependence of $\omega_{N,0}$ and $\tau_{N,0}$.[5] It is seen that η_1^- cuts off at lower pressures than does η_2^-, and that it changes sign at high H/p. This behavior can be understood from the frequency weight factors $\rho_1^-(\omega)$ and $\rho_2^-(\omega)$ in Fig. 2. The comparison is complicated by the fact that Fig. 2 refers to a fixed field value, whereas in Fig. 3, as in the experimental results, each curve is essentially a plot against H since p is constant. Clearly, however, the lower frequencies contribute at higher H/p. In particular the negative part of the $-\eta_1^-$ curve occurring at high H/p corresponds to the negative low-frequency part of $\rho_1^-(\omega)$ due to the band of negative frequencies in ρ_1. The negative peak in $-\eta_1^-$ is associated with those orientations of $\vec{J}$ having θ approximately 45°, whereas the positive peak is associated with the corresponding orientations in the lower hemisphere, namely, $\theta \sim 135°$. For $\omega_2 > 2^{1/2}\omega_L$ the directions of the precession of $\vec{J}$ are opposite for the two cases, and two peaks (positive and negative) are resolved because the magnitudes of the two precession frequencies differ by $2^{1/2}\omega_L$. The fact that the positive and negative peaks have different heights in Fig. 3 is due to the fact that the independent variable is H, rather than p. In a plot against $1/p$, at constant H, they would have comparable heights for not too small field strengths.

The complete H/p curves for the transverse coefficients can be obtained by adding the $\sigma = \pm 1$ contributions, given by Eq. (11), to the $\sigma = 0$ contributions shown in Fig. 3. No new parameters are required, but it is important, in evaluating expression (11), not to neglect quantities of order N^{-1} relative to 1 since the $\sigma = +1$ and $\sigma = -1$ contributions are of opposite sign and cancel in first order. The origin of the net $\sigma = \pm 1$ contribution is that this cancellation is not exact since the degeneracy $(2J+1)$, the magnitude of the Larmor frequency, and (very importantly) the relaxation times $\tau_{N\sigma} \propto \vec{J}^2$, all differ between $\sigma = \pm 1$ $(J = N \pm 1)$. A more detailed qualitative discussion is given in Ref. 5. The calculated $\sigma = \pm 1$ contribution is almost exactly the same for η_1^- and η_2^- apart from the displacement on the H/p axis, whereas experimentally the feature in η_1^- is slightly smaller, perhaps reflecting an over-all difference in scale.

The complete calculated H/p curves for the transverse coefficients, including the theoretical $\sigma = \pm 1$ contributions, are shown in Figs. 4(a) and 4(b). The experimental results of Hulsman *et al.*[3] are shown for comparison on the same scale. The minima in η_1^- at high H/p are somewhat larger experimentally than theoretically. Otherwise, the agreement is quite detailed. The spacing between the curves for sucessive pressures, and the relative heights, which are not at all the same for the two coefficients, are almost exactly reproduced in both cases. Such detailed agreement depends sensitively on the exact N dependence of the intensity factors $g_{N,\sigma}$, i.e., on the exact weighting of the N average, and it supports the assumptions $\varphi_{N\sigma}$ independent of $\{N, \sigma\}$ and $\tau_{N\sigma} \propto \vec{J}^2$ of Eqs. (26) and (27). It is emphasized that the theory contains no empirical parameters to scale the anomalous effects nor, in fact, any scaling at all of the shapes of the curves. The parameter τ_0 merely scales the over-all H/p position, and is determined once and for all by the low-pressure limit.

Even Viscosity Coefficients

Figures 5(a) and 5(b) show the calculated H/p curves at several pressures for the $\sigma = 0$ part of the field effect on the corresponding even viscosity coefficients η_1^+ and η_2^+. The most interesting anomalous effects occur at pressures of the order of 4 Torr. Here the H/p curves for both η_1^+ and η_2^+ lie at higher H/p than those for zero pressure, and

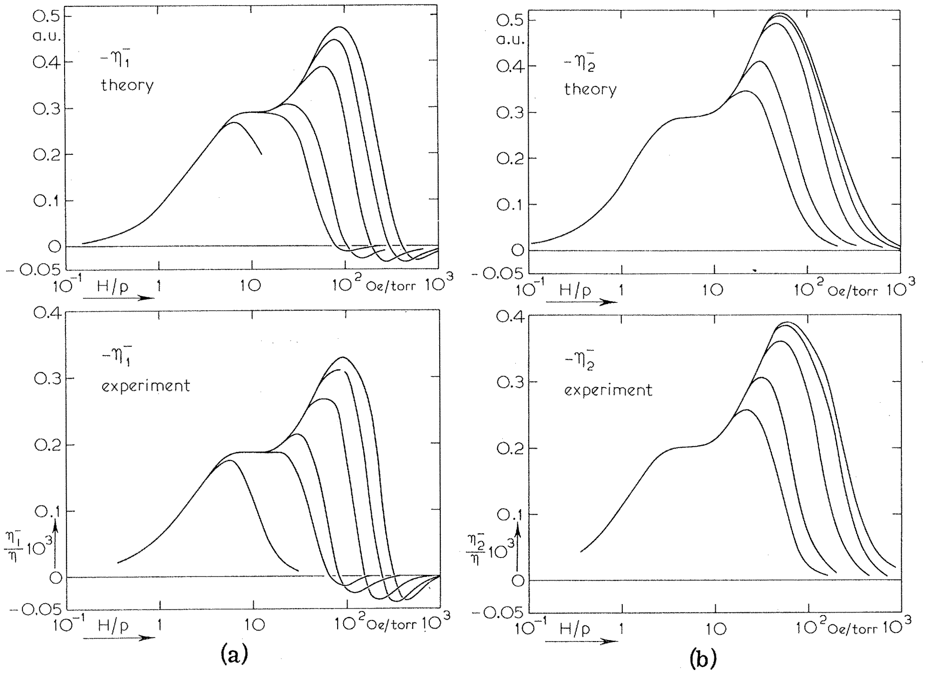

FIG. 4. (a) Complete H/p curves for the transverse viscosity coefficient $-\eta_1^-$ at pressures $p=4.1$, 6.0, 10.9, 31.6, 61.3, and 772 Torr. Top: theoretical curves (relative intensity scale). The full curve for 772 Torr is not shown because the calculation of the $\sigma=\pm 1$ contribution is valid for low fields only. Bottom: Experimental results, after Hulsman *et al*. (Ref. 3). (b) Theoretical and experimental (Ref. 3) H/p curves for the transverse viscosity coefficient $-\eta_2^-$. Same pressures as in (a) (except 772 Torr), and same relative intensity scale.

the forms of the curves have been modified in quite distinct ways. The calculated curve for η_2^+ at 4.1 Torr has a very slow final approach to saturation. This can be understood from Fig. 2, which shows that $\rho_2^+(\omega)$ gives a heavy weighting to very small frequencies. The H/p curve for η_1^+ at 4.1 Torr shows a double step (so that the complete H/p curve, including the $\sigma=\pm 1$ contribution will show a triple step). The origin of the double step is clear from the bimodal form of $\rho_1^+(\omega)$ seen in Fig. 2. The steps are resolved in spite of the averaging over multiplets. There is at least a suggestion of a double step in Hermans's[7] experimental results for the thermal-conductivity coefficient $\lambda_{\parallel}$ at 4.07 Torr. However, the existence and the complexity of the anomalous "pressure dependence" of the even coefficients in this low-pressure region has not been appreciated hitherto. At still lower pressures $p \sim 0.1$ Torr, $-\Delta\eta_1^+$ approaches saturation normally, but subsequently falls off by about 1% before reapproaching saturation. The reason for this behavior is that, for $p \sim 0.1$ Torr, the band of frequencies about $\omega_L - 0.7\omega_2$, which becomes negative at higher fields, only passes through zero after saturation has been reached. In other words, there is a group of energy levels whose separation decreases with increasing field after saturation has been attained.

At higher pressures (roughly $p > 10$ Torr for η_1^+, $p > 30$ Torr for η_2^+) the H/p curves are displaced progressively in the opposite direction to the left of the curve for $p=0$, and the forms once again become relatively simple. The reason for this behavior is simply that the quadratic term dominates, giving an approach to saturation as H^2/p. At 760 Torr the second-order perturbation approximation to the energy levels is inadequate long before saturation is reached. It is possible to make accurate

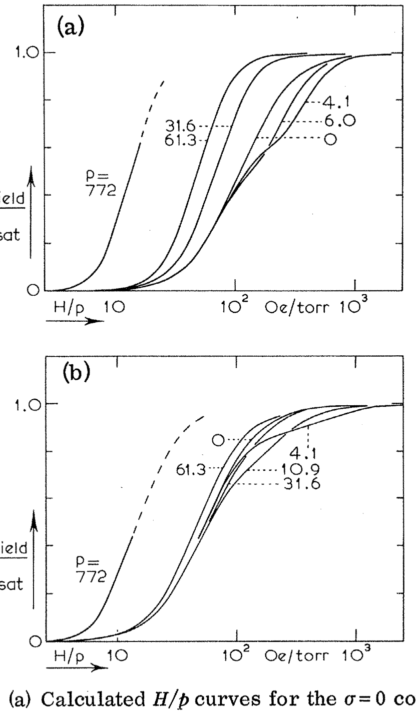

FIG. 5. (a) Calculated H/p curves for the $\sigma=0$ contribution to the even viscosity coefficient η_1^+. Note the step at 4.1 Torr. (b) Calculated H/p curves for the $\sigma=0$ contribution to the even viscosity coefficient η_2^+. Note the slow final approach to saturation at 4.1 Torr.

calculations, but unnecessary for the qualitative picture, which remains that of a progressively more rapid approach to saturation with increasing pressure. This higher-pressure behavior has now been recognized experimentally (see Fig. 20 in Hermans *et al.*[7]). At still higher pressures (a few atmospheres) the true Paschen-Back region of field strengths is reached before saturation, and the saturation values of $|\Delta\eta_{\mu}^{+}/\eta|$ must then decrease.[9]

V. DISCUSSION

For the thermal conductivity, the quantitative calculations would differ somewhat because of the completely elastic contribution to the collision integrals involving the relevant correlated polarizations, $\vec{W}|N\sigma m\rangle\langle N\sigma m'|$ or $\vec{W}\mathbf{Y}^2(\vec{J})$. The completely elastic contribution to τ^{-1} is J independent, and tends to decrease the J dependence of the intensities and hence to decrease the anomalous effects to which the high N shells contribute most. However, the smaller value of τ implies larger field values for a given pressure, and this tends, on the contrary, to increase the anomalous effects. The qualitative discussion, however, is similar to that for the viscosity. The thermal-conductivity coefficient $\lambda_{\parallel}$ depends on $\frac{1}{3}[\rho_0+2\rho_1^{+}f^{+}(\omega\tau)]$, whereas $\lambda_{\perp}$ and λ_{tr} depend on $\frac{1}{3}[\rho_1^{+}f^{+}(\omega\tau)+2\rho_2^{+}f^{+}(2\omega\tau)]$ and $\frac{1}{3}[\rho_1^{-}f^{-}(\omega\tau)+2\rho_2^{-}f^{-}(2\omega\tau)]$, respectively. Experimentally, the anomalies for the even effects at room temperature appear comparable to those for η_1^{+} and η_2^{+}, those for $\lambda_{\parallel}$ being, as they should, more pronounced than those for $\lambda_{\perp}$ (Hermans,[7] Fig. 18). For the transverse coefficient, the H/p curve of Gorelik *et al.*[13] for $p=5$ Torr at $t\sim 90\ ^{\circ}\mathrm{C}$ appears to show some cutting off on the right-hand side. At 77 °K, however—the temperature of Hermans's measurement[14]—the anomalous effects should be small.

The striking agreement of our calculated transverse viscosity coefficients with the measurements of Hulsman *et al.* supports uncoupled theory generally, and also the particular assumptions that $\varphi_{N\sigma}$ is multiplet independent and that $\tau_{N\sigma}$ is proportional to $\vec{J}^2$ for the viscosity polarization. These are Axioms VI and VII in Ref. 5. With a constant τ the calculated anomalous effects are too small at the same pressures. The assumption $\tau_{N,\sigma}\propto\vec{J}^2$ agrees not only with the anomalous pressure effects discussed here, but also with the narrowness of the transverse $\sigma=0$ peaks in the low-field limit, and with the intensity of the low-field $\sigma=\pm1$ feature.[5]

The difference between the forms of the H/p curves for η_1^{-} and η_2^{-} has been shown to reflect the different selections from the frequency spectrum, determined by the weight factors $|Y^{(2)1}(\theta,\phi)|^2$ and $|Y^{(2)2}(\theta,\phi)|^2$. The experimental results therefore give a rather direct illustration of the dependence of the internal-state contributions to the viscosity on the $\mathbf{Y}^2(\vec{J})$ polarizations.

The effects discussed here require the linear and quadratic splittings to be comparable in magnitude. In principle, the same effects could be seen in the transport coefficients of diamagnetic diatomic polar molecules, in the presence of colinear electric, and magnetic fields. The field strengths would have to be such that the second-order Stark effect is comparable to the linear rotational Zeemann effect.

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APPENDIX

It is sufficient to consider oxygen as conforming rigorously to Hund's case (b) and also, in calculating the $\sigma=0$ energies to second-order in the field, to neglect the splitting between the $\sigma=\pm1$ multiplets. For large N, the splitting between the $\sigma=\pm1$ multiplets tends to $2Nc_{sr}=-0.016\ N\ \mathrm{cm}^{-1}$, where c_{sr} is the spin-rotation interaction constant (whose spectroscopic notation is γ), which is small for the relevant N values compared to the larger $\lambda=2\text{-cm}^{-1}$ separation between $\sigma=0$ and the mean of the $\sigma=\pm1$ energies, which is due to the spin-spin interaction primarily.[15] Actually only terms of the order of $(Nc_{sr}/\lambda)^2$ are neglected. The matrix of the Zeemann interaction $\mathcal{H}_Z=-\gamma_s\vec{H}\cdot\vec{S}$ between the $\sigma=\pm1$, 0 levels of given $m=m_J$ and N is

$$\langle NS\sigma m|\mathcal{H}_Z|NS\sigma' m\rangle=-\gamma_s\hbar H\begin{array}{c} \\ \left(\begin{array}{ccc}(m/N+1) & 0 & H_{1,0}\\ 0 & -(m/N) & H_{-1,0}\\ H_{1,0} & H_{-1,0} & [m/N(N+1)]\end{array}\right)\end{array}\begin{array}{c}\sigma\\ 1\\ -1\\ 0\end{array}, \tag{A1}$$

where

$$H_{1,0}=[(N/2N+1)(1-(m/N+1)^2)]^{1/2},$$

$$H_{-1,0}=[(N+1/2N+1)(1-(m/N)^2)]^{1/2},$$

and second-order perturbation theory then gives

Eq. (16). This matrix may also be written, approximately,

$$-\gamma_s\hbar H\begin{pmatrix} \cos\theta & 0 & 2^{-1/2}\sin\theta \\ 0 & -\cos\theta & 2^{-1/2}\sin\theta \\ 2^{-1/2}\sin\theta & 2^{-1/2}\sin\theta & \cos\theta/|N| \end{pmatrix}, \qquad \text{(A2)}$$

where $\cos\theta = m/(\vec{N}^2)^{1/2}$, which gives Eq. (17) directly.

The $\sigma = 1$ and $\sigma = -1$ multiplets are not mixed directly by the field [cf. (A1) and (A2)], since the vector interaction $\vec{H}\cdot\vec{S}$ cannot mix states differing by $\Delta J = 2$. They are mixed only in second order through interaction with the distant $\sigma = 0$ levels. The formula corresponding to Eq. (17) is therefore more complicated, namely,

$$E_{\sigma=\pm1}(\theta) = \overline{E} + [\,\gamma_s\hbar H/2|N|\,]\cos\theta - [(\gamma_s\hbar H)^2/2\lambda]\sin^2\theta$$
$$\pm\{[\delta(N) - (\gamma_s\hbar H)\cos\theta]^2$$
$$+[(\gamma_s\hbar H)^2\sin^2\theta/2\lambda]^2\}^{1/2}\,. \qquad \text{(A3)}$$

Here $\overline{E} = \frac{1}{2}(H^{(0)}_{1,1} + H^{(0)}_{-1,1})$ is the mean zero-field position, whereas $\delta(N) = \frac{1}{2}(H^{(0)}_{1,1} - H^{(0)}_{-1,-1})$ gives the separation between $\sigma = 1$ and $\sigma = -1$ at zero field. For $\delta(N)$, the Schlapp[16] formula should be sufficient. For $N = 5$, the $\sigma = \pm 1$ multiplets are very nearly degenerate (cf. Tinkham and Strandberg[12]).

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Density Operator of Unpolarized Radiation

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The general form of the density operator for unpolarized radiation is obtained. It is shown that if two orthogonally polarized components of unpolarized radiation are statistically independent, the radiation is necessarily chaotic. It is also shown that the procedure currently being used for studying interactions of unpolarized radiation is not correct, and that Stokes's parameters do not correctly specify the unpolarized state of radiation.

I. INTRODUCTION

The concept of polarization of radiation is an old one. It was realized long ago that the natural light is not polarized. A natural (or unpolarized) beam of light is traditionally defined[1] as one whose any two orthogonal plane-polarized components have statistically independent phases. A consequence of this definition (also borne out experimentally for natural light) is[2,3] that (i) any plane-polarized component has the same intensity and that (ii) this intensity is unaltered on introducing an arbitrary