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Electric Dichroism Studies of Macromolecules in Solutions. I. Theoretical Considerations of Electric Dichroism and Electrochromism

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Abstract: We have generalized and expanded a semiclassical treatment of polarized absorption of molecules oriented in a uniform electric field to analyze the effects of very high electric fields and examined specifically interactions due to changes in electrooptic properties resulting from electronic excitation; particular emphasis has been placed on the behavior of rigid macromolecules having axial symmetry. The variation with field strength of two experimentally measurable parameters, the *reduced dichroism* and the *reduced electrochromism*, have been calculated. The former is related both to the structural parameters of the molecule through its permanent electric dipole moment and polarizability and to its optical *and* structural properties through the magnitude and orientation of the transition moments associated with resonant absorption frequencies. The latter is, however, *independent* of the magnitude or direction of the transition moments and depends only on differences between the electrical properties in the ground and excited electronic states. Both depend on the degree of orientation achieved. *Electrochromism*, originally predicted by Platt,[1] is expected to be a small but observable effect. When the applied field is small and the orientation results from the interaction of the field with the permanent or induced molecular dipole moment, the *reduced electrochromism* is the same as that obtained by Liptay and Czekalla. At high fields, we find that the dependence of the reduced dichroism on the field strength is very much a function of the anisotropic electric properties of the molecules: for a molecule whose polarizability (in the ground state) may be described by a prolate ellipsoid of revolution, in addition to quadratic terms in E, a linear term appears; for oblate ellipsoids the corresponding term is independent of field strength. When the optical excitation does not itself produce appreciable changes in the dielectric properties of the molecules, the observed *dichroism* at saturating fields directly and simply relates the orientation of the transition moment to a molecular axis.

One of the most powerful methods available for studying the structure and physical behavior of macromolecules is the measurement of the absorption of linearly polarized light by an ensemble of oriented molecules. If the orientation of the plane of polarization with respect to a symmetry axis of the molecule is known, then the relative absorption in two or more directions, that is, the dichroism or pleochromism, is a measure of the orientation of the chromophore in the macromolecule. For studies in solution, orientation produced by pulsed or static electric fields can generally be greater than that produced by flow or magnetic fields and should be the method of choice whenever the electric field does not itself induce chemical or structural changes. Many synthetic polymers as well as biological macromolecules do contain one or more symmetry axes and are stable in the strong field required to produce significant orientation. The orientation is produced as a result of the interaction between the field and the permanent molecular electric dipole, and/or the polarizability tensor, and the transition electric dipole of each molecule. If such an oriented molecule is illuminated with linearly polarized light whose wavelength is appropriate to excite the chromophore from the ground state to an excited state, the molecule should, in general, show selective absorption because the absorption coefficient of polarized light perpendicular to the direction of the electric field is now different from that of light parallel to it.[2] This is the phenomenon generally accepted as electric dichroism, the measurement of which was first carried out for *p*-nitrosodimethylaniline in hexane by Kuhn,

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(1) J. R. Platt, *J. Chem. Phys.*, **34**, 862 (1961).

(2) F. Dörr, *Angew. Chem., Int. Ed. Engl.*, **5**, 478 (1966).

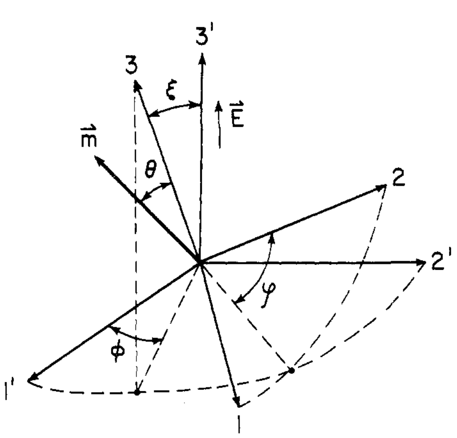

Figure 1. Coordinate systems, definition of eulerian angles, and the direction of transition moment unit vector *m*. The axes 1, 2, and 3, and 1', 2', and 3', respectively represent the molecule-fixed and the laboratory-fixed coordinate systems. External field *E* is applied along the 3' axis. θ is the angle between the direction of the transition moment and the symmetry axis of the molecule.

et al.[3] Although some experimental work has lately been reported on the electric dichroism of such polymers as deoxyribonucleic acid (DNA),[4-8] DNA complexed with various dyes,[5,7,8] deoxyribonucleohistone[9] and its complex with dyes,[5,9,10] ribonucleic acid in ribosomes,[11] polyamino acids[12,13] and other synthetic polymers,[7a,14] and spinach quantasomes,[15] no theoretical formulation of electric dichroism applicable to these macromolecular systems over the entire range of practical electric field strengths has appeared.

Recently Liptay and Czekalla were able to formulate a theory of electric dichroism for weak electric fields[16,17] and reported some experimental results for a number of small molecules.[18] Since it has been shown that the orientation of rigid macromolecules in general does not necessarily depend on the square of the applied electric field strength (the Kerr law is obeyed only in extremely weak fields) but tends to approach saturation,[19-21] any extended theory of the electric dichroism must cover the field dependence at any arbitrary field strength. Just as the more familiar circular dichroism bears a close relationship to optical rotatory dispersion,[22] electric dichroism is related in a similar way to electric birefringence.

In this paper we present a more general theory for electric dichroism taking under consideration different molecular models, the effect at any given field strength on the wavelength shift of an absorption band, and the dependence of the effect on the field strength up to saturation. The present theory is based on the earlier work by Liptay and Czekalla[16,17] and follows the theories of electric birefringence which have been well developed for macromolecular systems.[23] We confine ourselves at present to steady-state (or equilibrium) electric dichroism and do not discuss transient electric dichroism. We will elsewhere report electric dichroism measurements of some typical macromolecular systems and compare them with the present theory.

Theoretical Treatment

Upon application of an external homogeneous electric field to a macromolecular solution, the total energy of an electrically anisotropic macromolecule becomes dependent on the orientation of the molecule toward the field. The energy of the molecule in the *ns*-state may be written as

$$W_{ns} = W_{ns}^0 - E\sum_i ({}^{ns}\mu)_i l_i - \frac{E^2}{2}\sum_{i,j} ({}^{ns}\alpha)_{ij} l_i l_j \qquad (1)$$

where W_{ns} and W_{ns}^0 are respectively the total energy of the molecule in the *s*th substate of the *n*th electronic state in the presence and absence of an external electric field. $({}^{ns}\mu)_i$ and $({}^{ns}\alpha)_{ij}$ are respectively the components of the permanent electric dipole moment vector ${}^{ns}\boldsymbol{\mu}$ and of the electric polarizability tensor ${}^{ns}\alpha$ of the molecule (i = 1, 2, and 3) with reference to the molecule-fixed Cartesian coordinate system. l_i is the direction cosine, which defines the molecular orientation toward the field, between the molecule-fixed coordinate directions and the direction of the external field in the laboratory-fixed coordinate system (Figure 1). E is the effective field strength at the point of the molecule; however, no distinction is made here between the external and effective electric fields (for details, see ref 20). In this treatment, the molecules are regarded as point particles insofar as the effective field is concerned. When there are fixed charges on the macromolecule our model is applicable only if the charges behave (so far as their static or equilibrium properties are concerned) similarly to the valence electronic charge neutralized by the positive atomic nuclei. When the effect of the field on the neutralizing counterions is different, then the conductance of the solution and other factors may enter.[24] However, as a practical matter, when a polyelectrolyte has ionizable groups distributed centrosymmetrically throughout the polymer chain (unlike the situation in amphoteric proteins), solutions of polyelectrolytes adjusted to very low ionic conductance will probably not behave much differently from solutions of neutral macromolecules in nonconducting solvents so far as the static or equilibrium dichroism is concerned. Since we are not concerned with

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(23) For reviews see (a) C. T. O'Konski in "Encyclopedia of Polymer Science and Technology," Vol. 9, Wiley, New York, N. Y., 1968, p 551; (b) K. Yoshioka and H. Watanabe in "Physical Principles and Technique of Protein Chemistry," Part A, S. Leach, Ed., Academic Press, New York, N. Y., 1969, p 335.
(24) Recent efforts to examine these effects on molecular orientation include those of G. Schwarz, *Z. Phys. Chem. (Frankfurt am Main)*, **19**, 286 (1959), and C. T. O'Konski and S. Krause, *J. Phys. Chem.*, **74**, 3243 (1970).

dynamic properties which may be quite different even in solutions of low ionic conductance, we can expect the theory developed here to be useful for most electric dichroism measurements on macromolecules in solutions of high resistivity.

A. The Model of a Macromolecule in the Electronic Ground State. As a theoretical model a cylindrically symmetric macromolecule with the symmetry axis designated as the 3 axis (Figure 1) has been chosen. The electric properties of this model in the ground state ($n = g$) may be specified with both $({}^{gs}\mu)_i$ and $({}^{gs}\alpha)_{ii}$ where ${}^{gs}\mu = {}^{gs}\mu_3$ and ${}^{gs}\mu_1 = {}^{gs}\mu_2 = 0$ and ${}^{gs}\alpha_{11} = {}^{gs}\alpha_{22} \neq {}^{gs}\alpha_{33}$. Since the electric molecular polarizability along the transverse axis (the 1 or 2 axis) is either smaller or larger than, or equal to, that along the symmetry axis, the electric polarizability anisotropy $({}^{gs}\alpha_{33} - {}^{gs}\alpha_{11})$ may either be positive, negative, or zero. When it is positive the model is the one adopted by O'Konski, *et al.*[20] (hereafter denoted as prolate ellipsoid model[25]), whereas when it is negative, the model is that chosen by Shah[21] (hereafter denoted as oblate ellipsoid model). For real molecules, these models respectively represent molecules which may be approximated as prolate ellipsoids (or cylinders) and as oblate ellipsoids of revolution (or disks).[25] In the presence of an external field, the orientation potential energy ΔW may be written for the ground state from eq 1.

$$\Delta W = W_{gs} - W_{gs}{}^0 = -{}^{gs}\mu_3 E \cos \xi - \frac{E^2}{2}[({}^{gs}\alpha_{33} - {}^{gs}\alpha_{11}) \cos^2 \xi + {}^{gs}\alpha_{11}] \quad (2)$$

As previous workers have done, we assume for these models that (1) the macromolecules are rigid in solution; (2) the three principal axes for optical and electric properties coincide; (3) the solution is so dilute that no intermolecular interaction occurs; (4) the macromolecular system is monodisperse; (5) on excitation the electronic configuration of a chromophore changes, but the nuclear configuration remains unchanged; and (6) there is no solvation effect on the ground state electronic configuration of the macromolecule.

B. The Distribution of Molecular Orientation. The mean transition probability of a molecule in an ensemble of like molecules with statistically distributed orientations for the incident light polarized parallel to or perpendicular to the external field, $\Pi_\parallel$ or $\Pi_\perp$, is given in eq 3,[17] where ΔW is the interaction energy term

$$\Pi_{\parallel,\perp} = \frac{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \Pi_{\parallel,\perp} \exp(-\Delta W/kT) \sin \xi \, d\xi d\psi d\phi}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \exp(-\Delta W/kT) \sin \xi \, d\xi d\psi d\phi} \quad (3)$$

of eq 2.

Taking into account all assumptions and appropriate approximations as described above, eq 2 may be rewritten as follows

$$\Delta W/kT = -\beta\mu - \gamma u^2 - (\alpha_\parallel E^2/2kT) \quad (4)$$

where

$$\beta = \mu_3 E/kT, \quad u = \cos \xi, \quad \gamma = E^2(\alpha_{33} - \alpha_{11})/2kT \quad (5)$$

and $\gamma > 0$ for prolate ellipsoids, $\gamma = 0$ for spheres, and $\gamma < 0$ for oblate ellipsoids.

After straightforward but tedious integral calculations, the parallel and perpendicular transition probabilities are given as shown in eq 6 and 7.

$$\begin{aligned}
\Pi_\parallel = \frac{B\epsilon}{4\bar{\nu}}\Bigg\{ & 2\left[(m_1{}^2 + m_2{}^2) - (m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right] + \\
& \frac{E}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[4m_3{}^2\Delta\mu_3\frac{I_5}{I_8} + 2\{(m_1{}^2 + m_2{}^2)\Delta\mu_3 + 2m_3(m_1\Delta\mu_1 + m_2\Delta\mu_2)\}\left(\frac{I_4 - I_5}{I_8}\right)\right] + \\
& \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[\left\{\frac{1}{2}(3m_1{}^2 + m_2{}^2) + \frac{1}{2}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} - (3m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\alpha_{11} + \right. \\
& \left\{\frac{1}{2}(m_1{}^2 + 3m_2{}^2) + \frac{1}{2}(m_1{}^2 + 3m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} - (m_1{}^2 + 3m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\alpha_{22} + \\
& \left\{2(m_1{}^2 + m_2{}^2)\frac{I_7}{I_8} - 2(m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\alpha_{33} + m_1m_2(\Delta\alpha_{12} + \Delta\alpha_{21})\left(1 - \frac{I_7}{I_8}\right) + \\
& \left.\{4m_1m_3(\Delta\alpha_{13} + \Delta\alpha_{31}) - m_1m_2(\Delta\alpha_{12} + \Delta\alpha_{21}) + 4m_2m_3(\Delta\alpha_{23} + \Delta\alpha_{32})\}\frac{I_7 - I_3}{I_8}\right] + \\
& \frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}^2}\right] \times \\
& \left[\left\{\frac{1}{2}(3m_1{}^2 + m_2{}^2) + \frac{1}{2}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} - (3m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\mu_1{}^2 + \right. \\
& \left\{\frac{1}{2}(m_1{}^2 + 3m_2{}^2) + \frac{1}{2}(m_1{}^2 + 3m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} - (m_1{}^2 + 3m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\mu_2{}^2 + \\
& \left\{2(m_1{}^2 + m_2{}^2)\frac{I_7}{I_8} - 2(m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\mu_3{}^2 + 2m_1m_2\Delta\mu_1\Delta\mu_2\left(1 + \frac{I_3 - 2I_7}{I_8}\right) + \\
& \left.\left. 8(m_1m_3\Delta\mu_1\Delta\mu_3 + m_2m_3\Delta\mu_2\Delta\mu_3)\left(\frac{I_7 - I_3}{I_8}\right)\right]\right\}
\end{aligned} \quad (6)$$

---

[25] In this paper the terms prolate and oblate ellipsoids of revolution are used to describe the electric polarizability anisotropies of the macromolecules to which the appropriate theoretical considerations apply. They need not be coincident with hydrodynamic or structural shapes but, in many cases, do very closely approximate the latter, since the electric polarizability in any given direction is connected (taking into account differences in bonding or hybridization) with the electric charge displacement along the same direction. In a helical macromolecule in particular, the molecular polarization is rather closely related to the polarizability per monomeric unit and thus to the structural and hydrodynamic shapes. In any event, no loss of rigor is involved, but clarity requires that the terms prolate and oblate ellipsoids be defined as electrooptic rather than structural properties.

$$
\begin{aligned}
\Pi_{\perp} = \frac{B}{4}\frac{\epsilon}{\bar{\nu}}\Bigg\{ & \Bigg[(m_1^2 + m_2^2 + 2m_3^2) + \\
& (m_1^2 + m_2^2 - 2m_3^2)\frac{I_7}{I_8}\Bigg] + \\
& \frac{E}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\Bigg[(m_1^2 + m_2^2)\Delta\mu_3\left(\frac{I_9 + I_5}{I_8}\right) + \\
& 2m_3(m_1\Delta\mu_1 + m_2\Delta\mu_2 - m_3\Delta\mu_3)\left(\frac{I_5 - I_9}{I_8}\right)\Bigg] + \\
& \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\Bigg[\Bigg\{\frac{1}{4}(m_1^2 + 3m_2^2 + 4m_3^2) + \\
& \frac{1}{2}(m_1^2 - m_2^2 - 4m_3^2)\frac{I_7}{I_8} - \\
& \frac{1}{4}(3m_1^2 + m_2^2 - 4m_3^2)\frac{I_3}{I_8}\Bigg\}\Delta\alpha_{11} + \\
& \Bigg\{\frac{1}{4}(3m_1^2 + m_2^2 + 4m_3^2) - \frac{1}{2}(m_1^2 - m_2^2 + 4m_3^2)\frac{I_7}{I_8} - \\
& \frac{1}{4}(m_1^2 + 3m_2^2 - 4m_3^2)\frac{I_3}{I_8}\Bigg\}\Delta\alpha_{22} + \\
& \Bigg\{(m_1^2 + m_2^2 - 2m_3^2)\frac{I_3}{I_8} + \\
& (m_1^2 + m_2^2 + 2m_3^2)\frac{I_7}{I_8}\Bigg\}\Delta\alpha_{33} - \\
& \frac{1}{2}m_1m_2(\Delta\alpha_{12} + \Delta\alpha_{21})\frac{I_7}{I_8} + \\
& \Bigg\{\frac{1}{2}m_1m_2(\Delta\alpha_{12} + \Delta\alpha_{21}) - 2m_1m_3(\Delta\alpha_{13} + \Delta\alpha_{31}) - \\
& 2m_2m_3(\Delta\alpha_{23} + \Delta\alpha_{32})\Bigg\}\frac{I_7 - I_3}{I_8}\Bigg] + \\
& \frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}^2}\right] \times \\
& \Bigg[\Bigg\{\frac{1}{4}(m_1^2 + 3m_2^2 + 4m_3^2) + \frac{1}{2}(m_1^2 - m_2^2 - 4m_3^2)\frac{I_7}{I_8} - \\
& \frac{1}{4}(3m_1^2 + m_2^2 - 4m_3^2)\frac{I_3}{I_8}\Bigg\}\Delta\mu_1^2 + \\
& \Bigg\{\frac{1}{4}(3m_1^2 + m_2^2 + 4m_3^2) - \frac{1}{2}(m_1^2 - m_2^2 + 4m_3^2)\frac{I_7}{I_8} - \\
& \frac{1}{4}(m_1^2 + 3m_2^2 - 4m_3^2)\frac{I_3}{I_8}\Bigg\}\Delta\mu_2^2 + \\
& \Bigg\{(m_1^2 + m_2^2 - 2m_3^2)\frac{I_3}{I_8} + \\
& (m_1^2 + m_2^2 + 2m_3^2)\frac{I_7}{I_8}\Bigg\}\Delta\mu_3^2 - \\
& m_1m_2\Delta\mu_1\Delta\mu_2\left(1 + \frac{I_3 - 2I_7}{I_8}\right) - \\
& 4(m_1m_3\Delta\mu_1\Delta\mu_3 + m_2m_3\Delta\mu_2\Delta\mu_3)\left(\frac{I_7 - I_3}{I_8}\right)\Bigg]\Bigg\}
\end{aligned}
\tag{7}
$$

$m_i (i = 1, 2, 3)$ is the component of the unit vector **m** of the transition dipole moment along the three principal molecular-fixed axes. $B = 3000 \ln 10/hN_\mathrm{a}$; $\epsilon(\bar{\nu}) = \pi^0(\bar{\nu})h\bar{\nu}/(3000 \ln 10)$, and $\pi^0(\bar{\nu})$ = transition probability corresponding to the absorption band in the vicinity of the measuring frequency $\bar{\nu}$, and N_a = number of molecules/cm^3.

C. Calculation of Integrals. The integrals I_1 through I_9 are defined by the expressions in eq 8. These integrals appear in eq 6 and 7 for $\Pi_\parallel$ and $\Pi_\perp$ and thus in the final expressions for the reduced dichroism and electrochromism as ratios. Expressions for the integrated forms in terms of the molecular orienting force parameters β and γ are given in the Appendix both as general expressions (β and γ at arbitrary values) and for the special cases $\beta = 0$, $\gamma \neq 0$ and $\beta \neq 0$, $\gamma = 0$ for molecules whose electronic charge distributions are ellipsoids of revolution or spheres. Evaluation of the integrals is aided by the fact that upon substitution of eq 4 and 5 in the integral forms, I_8 reduces to a known definite integral and all other integrals can conveniently be expressed each as the ratio to I_8.

$$
\begin{aligned}
I_1 &= \int_0^\pi \sin^5\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi = I_8 - 2I_7 + I_3 \\
I_2 &= \int_0^\pi \sin^3\xi \cos^2\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi = I_7 - I_3 \\
I_3 &= \int_0^\pi \sin\xi \cos^4\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi \\
I_4 &= \int_0^\pi \sin^3\xi \cos\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi = I_9 - I_5 \\
I_5 &= \int_0^\pi \cos^3\xi \sin\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi \\
I_6 &= \int_0^\pi \sin^3\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi = I_8 - I_7 \\
I_7 &= \int_0^\pi \cos^2\xi \sin\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi \\
I_8 &= \int_0^\pi \sin\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi \\
I_9 &= \int_0^\pi \sin\xi \cos\xi \exp(-\Delta W/kT)\,\mathrm{d}\xi
\end{aligned}
\tag{8}
$$

For $\gamma > 0$

$$
I_8(\beta,\gamma) = \frac{e^{-\beta^2/4\gamma}}{\sqrt{\gamma}}\int_{t_1}^{t_2} e^{x^2}\mathrm{d}x = \frac{e^{\gamma}}{\sqrt{\gamma}}[e^{\beta}D(t_2) - e^{-\beta}D(t_1)] \tag{9}
$$

where $t_1 = -\sqrt{\gamma} + (\beta/2\sqrt{\gamma})$, $t_2 = \sqrt{\gamma} + (\beta/2\sqrt{\gamma})$, and $D(t)$ = Dawson's integral $\equiv e^{-t^2}\int_0^t e^{x^2}\,\mathrm{d}x$.

For $\gamma < 0$

$$
I_8(\beta,\gamma) = \frac{e^{-\beta^2/4\gamma}}{\sqrt{-\gamma}}\int_{t_1'}^{t_2'} e^{-x^2}\,\mathrm{d}x = \sqrt{-\frac{\pi}{4\gamma}}e^{-\beta^2/4\gamma}[\mathrm{erf}(t_2') + \mathrm{erf}(-t_1')] \tag{10}
$$

where $t_1' = -(\sqrt{-\gamma} + (\beta/2\sqrt{-\gamma}))$, $t_2' = \sqrt{-\gamma} - (\beta/2\sqrt{-\gamma})$, and $\mathrm{erf}(t')$ = error function $\equiv (2/\sqrt{\pi})\cdot$

$\int_0^{y'} e^{-x^2}$ dx. Three possible cases of orientation mechanisms are considered by choosing appropriate values of β and γ.

Case A. Polarizability Orientation. The orienting torque originates only from the electic polarizability anisotropy term in eq 2, *i.e.*, $\beta = 0$ and $\gamma \neq 0\,(\gtrless 0)$.

Case B. Permanent Dipole Orientation. The orienting torque is essentially due to the electric permanent dipole moment,[26] *i.e.*, $\beta \neq 0, \gamma = 0$.

Case C. Dipole–Polarizability Mixed Orientation. The orientation of molecules results from the interaction of both permanent dipole and polarizability anisotropy with external electric field. In each case, derivations have been given for the general expression for arbitrary values of β and γ as well as the two extremes where: (i) the electric field is relatively low so that β and $|\gamma|$ are much smaller than unity, and (ii) the electric field is high enough so that β and $|\gamma|$ are much larger than unity. For these extremes all integrals in eq 8 were expanded into series and the first few terms were retained. It should be noted that the so-called orientation function $\Phi(\beta,\gamma)$ introduced by O'Konski, *et al.*, for $\gamma > 0$[20] and by Shah for $\gamma < 0$,[21] respectively, bears a simple relationship to the integral $I_7(\beta,\gamma)/I_8(\beta,\gamma)$ in the present work

$$\Phi(\beta,\gamma) = \frac{3I_7(\beta,\gamma)}{2I_8(\beta,\gamma)} - \frac{1}{2} \quad (\gamma \gtrless 0) \tag{11}$$

Results

A. General Expressions for Electric Dichroism. By making the appropriate substitutions, the transition probability component parallel to the direction of the applied electric field is obtained; therefore a quantity which may designate the parallel (electric) dichroism is given as eq 12.

$$\left(\frac{A_{\parallel}}{A^0}\right)_{\beta,\gamma} = \frac{3\bar{\nu}}{B\epsilon(\bar{\nu})}\Pi_{\parallel}(\bar{\nu}) =$$

$$\frac{3}{4}\Bigg\{2\left[(m_1{}^2 + m_2{}^2) - (m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right] +$$

$$\frac{E}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[4m_3{}^2\Delta\mu_3\frac{I_5}{I_8} + 2\{(m_1{}^2 + m_2{}^2)\Delta\mu_3 +\right.$$

$$\left.2m_3(m_1\Delta\mu_1 + m_2\Delta\mu_2)\}\left(\frac{I_9 - I_5}{I_8}\right)\right] +$$

$$\frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[\left\{\frac{1}{2}(3m_1{}^2 + m_2{}^2) + \frac{1}{2}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} -\right.\right.$$

$$\left.(3m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\alpha_{11} +$$

$$\left\{\frac{1}{2}(m_1{}^2 + 3m_2{}^2) + \frac{1}{2}(m_1{}^2 + 3m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} -\right.$$

$$\left.(m_1{}^2 + 3m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\alpha_{22} +$$

$$\left.\left\{2(m_1{}^2 + m_2{}^2)\frac{I_7}{I_8} - 2(m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\alpha_{33}\right] +$$

$$\frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}^2}\right] \times$$

$$\left[\left\{\frac{1}{2}(3m_1{}^2 + m_2{}^2) + \frac{1}{2}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} -\right.\right.$$

$$\left.(3m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\mu_1{}^2 +$$

$$\left\{\frac{1}{2}(m_1{}^2 + 3m_2{}^2) + \frac{1}{2}(m_1{}^2 + 3m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8} -\right.$$

$$\left.(m_1{}^2 + 3m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\mu_2{}^2 +$$

$$\left\{2(m_1{}^2 + m_2{}^2)\frac{I_7}{I_8} - 2(m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\mu_3{}^2 +$$

$$2m_1m_2\Delta\mu_1\Delta\mu_2\left(1 + \frac{I_3 - 2I_7}{I_8}\right) +$$

$$\left.\left.8(m_1m_3\Delta\mu_1\Delta\mu_3 + m_2m_3\Delta\mu_2\Delta\mu_3)\left(\frac{I_7 - I_3}{I_8}\right)\right]\right\} \tag{12}$$

Similarly for the component perpendicular to the electric field, eq 13 applies, where $A_{\parallel}$ and $A_{\perp}$ are re-

$$\left(\frac{A_{\perp}}{A^0}\right)_{\beta,\gamma} = \frac{3\bar{\nu}}{B\epsilon(\bar{\nu})}\Pi_{\perp}(\bar{\nu}) =$$

$$\frac{3}{4}\Bigg\{\left[(m_1{}^2 + m_2{}^2 + 2m_3{}^2) + (m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_7}{I_8}\right] +$$

$$\frac{E}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[(m_1{}^2 + m_2{}^2)\Delta\mu_3\left(\frac{I_9 + I_5}{I_8}\right) +\right.$$

$$\left.2m_3(m_1\Delta\mu_1 + m_2\Delta\mu_2 - m_3\Delta\mu_3)\left(\frac{I_5 - I_9}{I_8}\right)\right] +$$

$$\frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\left[\left\{\frac{1}{4}(m_1{}^2 + 3m_2{}^2 + 4m_3{}^2) +\right.\right.$$

$$\frac{1}{2}(m_1{}^2 - m_2{}^2 - 4m_3{}^2)\frac{I_7}{I_8} -$$

$$\left.\frac{1}{4}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\alpha_{11} +$$

$$\left\{\frac{1}{4}(3m_1{}^2 + m_2{}^2 + 4m_3{}^2) - \frac{1}{2}(m_1{}^2 - m_2{}^2 + 4m_3{}^2)\frac{I_7}{I_8} -\right.$$

$$\left.\frac{1}{4}(m_1{}^2 + 3m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\alpha_{22} +$$

$$\left\{(m_1{}^2 + m_2{}^2 - 2m_3{}^2)\frac{I_3}{I_8} +\right.$$

$$\left.(m_1{}^2 + m_2{}^2 + 2m_3{}^2)\frac{I_7}{I_8}\right\}\Delta\alpha_{33} +$$

$$\frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar{\nu}}}{\mathrm{d}\bar{\nu}^2}\right] \times$$

$$\left[\left\{\frac{1}{4}(m_1{}^2 + 3m_2{}^2 + 4m_3{}^2) + \frac{1}{2}(m_1{}^2 - m_2{}^2 - 4m_3{}^2)\frac{I_7}{I_8} -\right.\right.$$

$$\left.\frac{1}{4}(3m_1{}^2 + m_2{}^2 - 4m_3{}^2)\frac{I_3}{I_8}\right\}\Delta\mu_1{}^2 +$$

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[26] To be precise, this case is only mathematically distinguishable, since a molecule with truly spherical polarizability will not have a permanent dipole moment; however, real molecules may frequently be approximated with this mechanism.

$$\left\{\frac{1}{4}(3m_1^2 + m_2^2 + 4m_3^2) - \frac{1}{2}(m_1^2 - m_2^2 + 4m_3^2)\frac{I_7}{I_8} - \frac{1}{4}(m_1^2 + 3m_2^2 - 4m_3^2)\frac{I_3}{I_8}\right\}\Delta\mu_2^2 + \left\{(m_1^2 + m_2^2 - 2m_3^2)\frac{I_3}{I_8} + (m_1^2 + m_2^2 + 2m_3^2)\frac{I_7}{I_8}\right\} \times \Delta\mu_3^2 - m_1m_2\Delta\mu_1\Delta\mu_2\left(1 + \frac{I_3 - 2I_7}{I_8}\right) - 4(m_1m_3\Delta\mu_1\Delta\mu_3 + m_2m_3\Delta\mu_2\Delta\mu_3)\left(\frac{I_7 - I_3}{I_8}\right)\Bigg]\Bigg\} \quad (13)$$

spectively the absorbance of light linearly polarized parallel and perpendicular to the direction of the external electric field, which, in turn is perpendicular to the propagation direction of the light. A^0 is the isotropic absorbance in the absence of the field and is independent of the plane of polarization of the incident light unless the absorbing system is naturally dichroic. All integrals in eq 12 and 13 depend on the sign of γ and should be used in the appropriate form as listed in the Appendix. Equations 12 and 13 are the basic expressions to be utilized in the study of electric dichroism of axially symmetric molecules, that is, with the assumptions $\mu_1 = \mu_2 = 0$, $\alpha_{11} = \alpha_{22}$, $\alpha_{ij} = 0$ if $i_{ij} \neq j$, and $\Delta\alpha_{ij} = \Delta\alpha_{ji} = 0$ if $i \neq j$. Although these expressions are rather complex and hardly tractable, they are directly linked with experimentally determinable quantities, $A_\perp$ and $A_\parallel$, and they may further be combined to yield simpler expressions from which desired molecular information can be extracted.

(1) Reduced Dichroism. The reduced dichroism is defined as in eq 14, where $|\mathbf{m}|^2 = m_1^2 + m_2^2 + m_3^2 = 1$.

$$\frac{\Delta\epsilon}{\epsilon^0} \equiv \frac{\epsilon_\parallel - \epsilon_\perp}{\epsilon^0} = \frac{A_\parallel - A_\perp}{A^0} = \frac{3}{4}\Bigg\{(1 - 3m_3^2)\left(1 - 3\frac{I_7}{I_8}\right) + \frac{E}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left[(1 - 3m_3^2)\Delta\mu_3\left(\frac{I_9}{I_8} - \frac{3I_5}{I_8}\right) + 6m_3(m_1\Delta\mu_1 + m_2\Delta\mu_2)\left(\frac{I_9}{I_8} - \frac{I_5}{I_8}\right)\right] + \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\Bigg[\left\{\frac{1}{2}(1 - 3m_3^2)\left(\frac{1}{2} - \frac{3I_7}{I_8} + \frac{5I_3}{2I_8}\right) - (1 - 3m_1^2)\left(\frac{1}{2} - \frac{I_7}{I_8} + \frac{I_3}{2I_8}\right)\right\}\Delta\alpha_{11} + \left\{\frac{1}{2}(1 - 3m_3^2)\left(\frac{1}{2} - \frac{3I_7}{I_8} + \frac{5I_3}{2I_8}\right) - (1 - 3m_2^2)\left(\frac{1}{2} - \frac{I_7}{I_8} + \frac{I_3}{2I_8}\right)\right\}\Delta\alpha_{22} + (1 - 3m_3^2)\left(\frac{I_7}{I_8} - \frac{3I_3}{I_8}\right)\Delta\alpha_{33} + \frac{E^2}{2h^2c^2}\left[\frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2} + \left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2\right] \times \left[\left\{\frac{1}{2}(1 - 3m_3^2)\left(\frac{1}{2} - \frac{3I_7}{I_8} + \frac{5I_3}{2I_8}\right) - (1 - 3m_1^2)\left(\frac{1}{2} - \frac{I_7}{I_8} + \frac{I_3}{2I_8}\right)\right\}\Delta\mu_1^2 + \left\{\frac{1}{2}(1 - 3m_3^2)\left(\frac{1}{2} - \frac{3I_7}{I_8} + \frac{5I_3}{2I_8}\right) - (1 - 3m_2^2)\left(\frac{1}{2} - \frac{I_7}{I_8} + \frac{I_3}{2I_8}\right)\right\}\Delta\mu_2^2 + (1 - 3m_3^2)\left(\frac{I_7}{I_8} - \frac{3I_3}{I_8}\right)\Delta\mu_3^2 + 3m_1m_2\Delta\mu_1\Delta\mu_2\left(1 + \frac{I_3}{I_8} - \frac{2I_7}{I_8}\right) + 12(m_1m_2\Delta\mu_1\Delta\mu_3 + m_2m_3\Delta\mu_2\Delta\mu_3)\left(\frac{I_7}{I_8} - \frac{I_3}{I_8}\right)\right]\Bigg\} \quad (14)$$

(2) Reduced Electrochromism. Since the mean transition probability at an angle of χ (χ is the angle between the plane of polarization of the radiation and direction of the electric field) is given by

$$\Pi_\chi(\bar\nu) = \Pi_\parallel(\bar\nu)\cos^2\chi + \Pi_\perp(\bar\nu)\sin^2\chi \quad (15)$$

and the dichroism in terms of absorbance is given by

$$\frac{A_\chi}{A^0} = \frac{A_\parallel}{A^0}\cos^2\chi + \frac{A_\perp}{A^0}\sin^2\chi \quad (16)$$

for $\cos^2\chi = {}^1/_3$ or $\chi = 54.735°$, eq 16 will be written as shown in eq 17. The reason for this nomenclature

$$\frac{A_{54.7}}{A^0} - 1 = \frac{1}{3}\left\{\frac{A_\parallel - A^0}{A^0} + \frac{2(A_\perp - A^0)}{A^0}\right\} = \frac{1}{3}\left(\frac{A_\parallel + 2A_\perp}{A^0}\right) - 1 = \frac{1}{4}\Bigg\{\frac{E^2}{hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left[\frac{4\Delta\mu_3}{E}\frac{I_9}{I_8} + (\Sigma\Delta\alpha_{ii})\left(1 - \frac{I_7}{I_8}\right) - \Delta\alpha_{33}\left(1 - \frac{3I_7}{I_8}\right)\right] + \left(\frac{E}{hc}\right)^2\left[\frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2} + \left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2\right] \times \left[\Delta\mu^2\left(1 - \frac{I_7}{I_8}\right) - \Delta\mu_3^2\left(1 - \frac{3I_7}{I_8}\right)\right]\Bigg\} \quad (17)$$

will be discussed later. Here it is simply noted that in distinction from the dichroism, this quantity is independent of the transition moment **m** or its components m_i ($i = 1, 2, 3$). It depends only on the electrical properties of the molecules in the ground and electronically excited states.

It should be noted that each ϵ represents the molar extinction coefficient and refers to the transition probability for an isolated band, *i.e.*, one in which substantially all the intensity arises from a single electronic transition. Cases where more than one electronic transition overlap and where vibronic bands of different polarization contribute to the apparent extinction will be considered elsewhere.

B. Expressions for Electric Dichroism at Extreme Electric Fields. From the general expressions given above, some special cases are easily derived and will be given below.

(1) Low Electric Fields ($\beta \ll 1, |\gamma| \ll 1$). The reduced dichroism due to the dipole-polarizability mixed orientation (case C) at very low field strength can be obtained up to E^2 terms, *i.e.*, β^2 and γ terms, of the integrals expanded into series for $\beta \ll 1$ and $|\gamma| \ll 1$ (Appendix, and by substituting them into eq 31). For both $\gamma > 0$ and $\gamma < 0$, eq 18 applies. Regardless of

$$\left(\frac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\ll 1} = \frac{1}{10}(3m_3^2 - 1)(\beta^2 + 2\gamma) + \frac{E^2}{10hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left(\frac{6\beta}{E}m_3\Sigma m_i\Delta\mu_i - \frac{2\beta\Delta\mu_3}{E} + 3\Sigma m_i^2\Delta\alpha_{ii} - \Sigma\Delta\alpha_{ii}\right) + \frac{E^2}{10h^2c^2}\times \left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right][3(\Sigma m_i\Delta\mu_i)^2 - \Sigma\Delta\mu_i^2] \tag{18}$$

the sign and magnitude of γ, the reduced electrochromism becomes that given in eq 19.

$$\frac{1}{3}\left(\frac{A_\parallel + 2A_\perp}{A^0}\right)_{\beta,|\gamma|\ll 1} - 1 = \frac{E^2}{6hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\left(\frac{2\beta\,\Delta\mu_3}{E} + \Sigma\Delta\alpha_{ii}\right) + \frac{E^2}{6h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\nu^2}\right]\Sigma\Delta\mu_i^2 \tag{19}$$

(2) High Electric Fields ($\beta \gg 1, |\gamma| \gg 1$). For sufficiently high electric fields, all orientation functions tend to approach saturation asymptotically and the degree of this approach is very much dependent on the macromolecular model (see the Discussion).

The reduced dichroism at high electric fields due to the polarizability–dipole mixed orientation is given in eq 20 for $\gamma > 0$.

$$\begin{aligned}\left(\frac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\gg 1} = \frac{3}{2}\Bigg\{&(3m_3^2 - 1)\left(1 - \frac{3}{\beta + 2\gamma}\right) + \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\Bigg[\frac{2\Delta\mu_3}{E}(3m_3^2 - 1)\left(1 - \frac{4}{\beta + 2\gamma}\right) + \frac{12m_3}{E}(m_1\Delta\mu_1 + m_2\Delta\mu_2)\left(\frac{1}{\beta + 2\gamma}\right) + \\ &(3m_3^2 - 1)\left\{\frac{1}{\beta + 2\gamma}(\Delta\alpha_{11} + \Delta\alpha_{22}) + \Delta\alpha_{33}\left(1 - \frac{5}{\beta + 2\gamma}\right)\right\}\Bigg] + \frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu_2}\right]\Bigg[(3m_3^2 - 1)\left\{(\Delta\mu_1^2 + \Delta\mu_2^2)\frac{1}{\beta + 2\gamma} + \right. \\ &\left.\Delta\mu_3^2\left(1 - \frac{5}{\beta + 2\gamma}\right)\right\} + 12m_3\Delta\mu_3(m_1\Delta\mu_1 + m_2\Delta\mu_2)\left(\frac{1}{\beta + 2\gamma}\right)\Bigg]\Bigg\}\end{aligned} \tag{20}$$

For $\gamma < 0$ and further if $(\beta/2|\gamma|) < 1$, eq 21 applies.

$$\begin{aligned}\left(\frac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\gg 1} = \frac{3}{4}\Bigg\{&(1 - 3m_3^2)\left(1 + \frac{3}{2\gamma}\right) + \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\Bigg[-\frac{\Delta\mu_3}{E}(1 - m_3^2)\left(\frac{\beta}{\gamma}\right) - \frac{6m_3}{E}(m_1\Delta\mu_1 + m_2\Delta\mu_2)\left(\frac{\beta}{\gamma}\right) + \\ &(1 - 3m_3^2)\left\{\left(\frac{1}{2} + \frac{3}{2\gamma}\right)\left(\frac{\Delta\alpha_{11} + \Delta\alpha_{22}}{2}\right) - \frac{\Delta\alpha_{33}}{2\gamma}\right\} - \left(\frac{1}{2} + \frac{1}{2\gamma}\right)\{(1 - 3m_1^2)\Delta\alpha_{11} + (1 - 3m_3^2)\Delta\alpha_{22}\}\Bigg] + \\ &\frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right]\times\Bigg[(1 - 3m_3^2)\left\{\left(\frac{1}{2} + \frac{3}{2\gamma}\right)\left(\frac{\Delta\mu_1^2 + \Delta\mu_2^2}{2}\right) - \frac{\Delta\mu_3^2}{2\gamma}\right\} - \\ &\left(\frac{1}{2} + \frac{1}{2\gamma}\right)\{(\Delta\mu_1^2 + \Delta\mu_2^2) - 3(m_1\Delta\mu_1 + m_2\Delta\mu_2)^2\} - \frac{6m_3\Delta\mu_3}{\gamma}(m_1\Delta\mu_1 + m_2\Delta\mu_2)\Bigg]\Bigg\}\end{aligned} \tag{21}$$

Equations for the reduced electrochromism may also be easily derived. At sufficiently strong field strengths, both electric dichroism and electrochromism depend on the molecular model, although the latter again does not involve the transition moment of the chromophore. It is noted that a term which is *dependent on the first order of the electric field strength E* now appears in the *reduced dichroism* expression for prolate ellipsoids, while the corresponding term is independent of the field strength for oblate ellipsoids in which the ground state interaction is predominantly through the polarizability anisotropy.

(3) Saturating Electric Fields. As the values of β and $|\gamma|$, or either of them become extremely large, *i.e.*, the field strength E is high enough to orient all molecules completely, all integrals in the Appendix approach unity for the positive values of γ and become zero for the negative values of γ. This is the case where essentially all molecules are lined up unidirectionally along the electric field and the dichroism expressions ultimately reduce to simple forms. For prolate ellipsoids (β and $\gamma > 0$), the reduced dichroism, the electrochromism, and the dichroic ratio become respectively

$$\left(\frac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\to\infty} = \frac{3}{2}(3m_3^2 - 1)\times\left\{1 + \frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left(\frac{2\Delta\mu_3}{E} + \Delta\alpha_{33}\right) + \frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right]\Delta\mu_3^2\right\} \tag{22}$$

$$\frac{1}{3}\left(\frac{A_{\parallel} + 2A_{\perp}}{A^0}\right)_{\beta,\gamma\to\infty} - 1 =$$

$$\frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left(\frac{2\,\Delta\mu_3}{E} + \Delta\alpha_{33}\right) +$$

$$\frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right]\Delta\mu_3{}^2 \qquad (23)$$

and

$$\left(\frac{A_{\parallel}}{A_{\perp}}\right)_{\beta,\gamma\to\infty} = \frac{2m_3{}^2}{1 - m_3{}^2} \qquad (24)$$

for oblate ellipsoids $\gamma < 0$

$$\left(\frac{A_{\parallel} - A_{\perp}}{A^0}\right)_{\beta,\gamma\to\infty} = \frac{3}{4}\Bigg\{(1 - 3m_3{}^2) +$$

$$\frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left[\frac{1}{4}(1 - 3m_3{}^2)(\Delta\alpha_{11} + \Delta\alpha_{22}) +\right.$$

$$\left.\frac{3}{2}(m_1{}^2\Delta\alpha_{11} + m_2{}^2\Delta\alpha_{22}) - \frac{1}{2}(\Delta\alpha_{11} + \Delta\alpha_{22})\right] +$$

$$\frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right] \times$$

$$\left[\frac{1}{4}(1 - 3m_3{}^2)(\Delta\mu_1{}^2 + \Delta\mu_2{}^2) +\right.$$

$$\left.\frac{3}{2}(m_1\Delta\mu_1 + m_2\Delta\mu_2)^2 - \frac{1}{2}(\Delta\mu_1{}^2 + \Delta\mu_2{}^2)\right]\Bigg\} \qquad (25)$$

and

$$\frac{1}{3}\left(\frac{A_{\parallel} - A_{\perp}}{A^0}\right)_{\beta,|\gamma|\to\infty} - 1 = \frac{E^2}{4hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}(\Delta\alpha_{11} + \Delta\alpha_{22}) +$$

$$\frac{E^2}{4h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\right)^2 + \frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right](\Delta\mu_1{}^2 + \Delta\mu_2{}^2) \qquad (26)$$

Here eq 23 and 26 show no direct contribution from the transition dipole but only the indirect effect of electronic excitation in producing changes in the charge distribution. The reduced dichroism for oblate ellipsoids ($\gamma < 0$) is not as simple as for prolate ellipsoids ($\gamma > 0$); in the former, there remain terms containing the contribution from the transition dipole moment components m_1 and m_2 even at the saturating electric field.

For oblate ellipsoids, however, a slightly simpler form may be derived.

$$\left(\frac{2A_{\perp} - 3A_{\parallel}}{A^0}\right)_{\beta,|\gamma|\to\infty} = (2m_3{}^2 - 1) +$$

$$\frac{E^2}{2hc}\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu}\left[\frac{m_3{}^2}{2}(\Delta\alpha_{11} + \Delta\alpha_{22}) -\right.$$

$$\left.(m_1{}^2\Delta\alpha_{11} + m_2{}^2\Delta\alpha_{22})\right] + \frac{E^2}{2h^2c^2}\left[\left(\frac{\mathrm{d}\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right)^2 +\right.$$

$$\left.\frac{\mathrm{d}^2\ln\frac{\epsilon}{\bar\nu}}{\mathrm{d}\bar\nu^2}\right]\left[\frac{m_3{}^2}{2}(\Delta\mu_1{}^2 + \Delta\mu_2{}^2) - (m_1\Delta\mu_1 + m_2\Delta\mu_2)^2\right] \qquad (27)$$

There appear two interaction terms; one between the transition dipole and the difference in electric polarizabilities between ground and excited states, and the other between the transition dipole and the differences in electric permanent dipole between ground and excited states. For this model of polar molecules, the optical property of the chromophore is not separable from the electric properties even when the molecules are completely oriented.

C. Numerical Calculation of Integrals I_3 through I_9. In order to determine the molecular electric properties of the electronic ground state, μ_3 and ($\alpha_{33} - \alpha_{11}$), from experimental dichroic data obtained at given electric field strengths, it is first necessary to compare the electric field dependence with a set of theoretical dichroism curves as a function of the external electric field and subsequently to evaluate variables β and γ. The expressions for the reduced dichroism and other quantities can all be expressed in terms of the ratios of the integrals, the denominator of which is always I_8, rather than the individual integrals in eq 8; therefore, I_8 was first computed with use of an IBM computer for positive as well as negative values of γ (see eq 9 and 10) as a function of $|\beta^2 + 2\gamma|$ at various ratios of β^2/γ as parameters. Since the integral contains well-known functions whose numerical values are tabulated in ref 27 for Dawson's integral and in ref 28 for the error function, these numerical tables were fully utilized and incorporated into the computer program.[29] With I_8 thus computed, the integral ratios defined in case C of the Appendix for arbitrary field strengths, were obtained at various ratios of β^2/γ for both positive and negative values of γ.

The results for I_7/I_8, the predominant contributor to the reduced dichroism whenever the derivative terms are zero or small, *e.g.*, near band maxima, are shown in Figure 2A where this parameter is plotted *vs.* $|\beta^2 + 2\gamma|$ for some typical values of $\beta^2/2\gamma$ as parameters.[30] The values of I_7/I_8 shown in Figure 2B were checked with the available values of $\Phi(\beta,\gamma > 0)$[31] and $\Phi(\beta,\gamma < 0)$[32] both of which are related to I_7/I_8 as shown by eq 11.

It is at once apparent that saturation values of the dichroism are reached most quickly, as the permanent moment is smaller and the anisotropy of induced moment is greater. Thus saturating orientation is achieved at lower field strengths for molecules with dipole moments small relative to the anisotropic polarizability.

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(27) M. Abramowitz and I. A. Stegun, Eds., "Handbook of Mathematical Functions," Dover Publications, New York, N. Y., 1965, p 319.

(28) National Bureau of Standards, "Tables of the Error Function and Its Derivative," Applied Math. Series 41, 2nd ed, U. S. Government Printing Office, Washington, D. C., 1954.

(29) We wish to thank Mr. R. Shrager and Mrs. M. McNeel of the Division of Computer Research and Technology, NIH, for developing the computer programs. In Figure 2, data are given for selected values as indicated. A much more extensive range of values can be made available for research use.

(30) Figures for the integral ratios I_9/I_8, I_5/I_8, and I_3/I_8 are available from the authors. In addition complete tables of the integrals over a wide range of the parameters can be made available.

(31) (a) K. Yomaoka, Ph.D. Thesis, University of California, Berkeley, Calif., 1964; (b) M. Matsumoto, H. Watanabe, and K. Yoshioka, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo*, 17, 173 (1963).

(32) M. J. Shah, IBM Technical Report, TR-02-250 (1963).

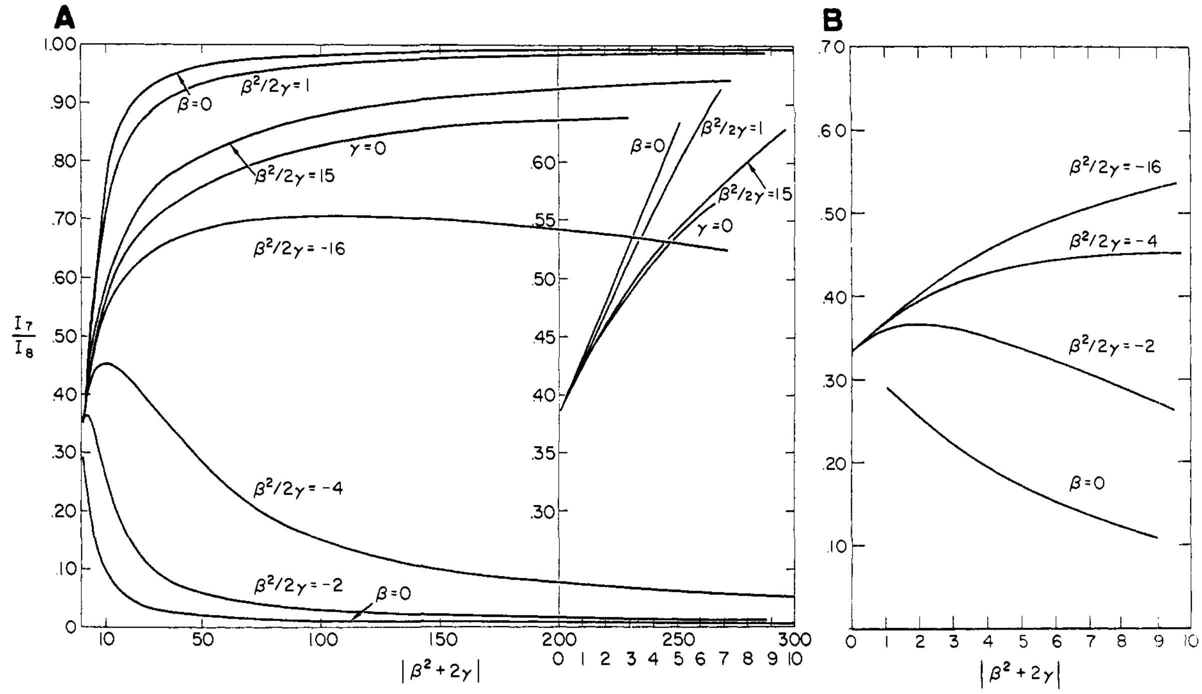

Figure 2. (A) I_7/I_8 for $|\beta^2 + 2\gamma|_{0\to300}$, $(\beta^2/2\gamma) \gtrless 0$; $|\beta^2 + 2\gamma|_{0\to10}$, $(\beta^2/2\gamma) > 0$; (B) $|\beta^2 + 2\gamma|_{0\to10}$, $(\beta^2/2\gamma) < 0$.

The area of nearly linear behavior with the square of the field strength is also greater for molecules whose orientation depends on ansisotropic polarizability. For example, in the insert in Figure 2, the curve for $\beta = 0$ (no permanent dipole moment) is linear up to $|\beta^2 + 2\gamma| = 5$ while for $\gamma = 0$ (no induced dipole moment) curvature sets in by the time $|\beta^2 + 2\gamma| = 2$. It should be pointed out that these values still cover a rather large range of practical cases. For example, the value of β^2 at field strengths of even 25,000 V/cm is about 4 for a polymer molecule having a moment of about 1000 D. For such a molecule with $\gamma > 0$, therefore quadratic dependence of the reduced dichroism over a rather large range of field strengths is expected unless γ is extraordinarily large. It is also interesting to observe in Figure 2 that as the anisotropic polarizability increases for oblate ellipsoids I_7/I_8 at first increases and then decreases with increasing field strength in the range where $\beta^2/2\gamma < -1$. No such behavior has yet been reported.[33]

Discussion

Electric dichroism as formulated in this work has clearly been shown to consist of two contributions: one is the orientational interaction between a homogeneous external electric field and the electrooptical properties of the molecular electronic ground state only, and the other is the inductive interaction between the electric field and the difference in the permanent electric dipole moments and polarizabilities of the molecule in the electronic ground and excited states. The formulas derived in the preceding sections are rather complex; however, they may be further simplified by making some reasonable assumptions with respect to the electrooptical properties and dimensions of molecules under investigation.

A. The Electric Dichroism Resulting from the Orientation Only. In this approximation the theory is applicable to molecules whose ground state electrooptical properties are very close to those of the excited state so that all $\Delta\mu_i$ and $\Delta\alpha_{ii}$ $(i = 1, 2, 3)$ can be approximated to be zero or otherwise very small compared with μ_3 and $|\alpha_{33} - \alpha_{11}|$ in the ground state. This approximation leaves only the first term in the reduced dichrosim expressions nonvanishing, while the higher order terms involving $\Delta\mu_i$ and $\Delta\alpha_{ii}$ vanish regardless of the electric field strength and of the values of β and $|\gamma|$. Under these circumstances, the electrochromism effect would be very small and probably could not be observed; hence, the isotropic absorbance in the absence of the field is equal to that in the presence of the field and is given as $A_0 = (A_\parallel + A_\perp)/3$.

Under these conditions, the specific parallel and perpendicular dichroism as defined in eq 14 and its perpendicular counterpart now become for both positive and negative values of γ

$$\left(\frac{A_\parallel - A^0}{A^0}\right)_{\beta,\gamma} = \left(\frac{\Delta\epsilon_\perp}{\epsilon}\right)_{\beta,\gamma} = (3m_3^2 - 1) \times \left[\frac{3I_7(\beta,\gamma)}{2I_8(\beta,\gamma)} - \frac{1}{2}\right] = (3m_3^2 - 1)\Phi(\beta,\gamma) \quad (28)$$

and

$$\left(\frac{A_\perp - A_\parallel}{A^0}\right)_{\beta,\gamma} = \left(\frac{\Delta\epsilon_\perp}{\epsilon}\right)_{\beta,\gamma} = \frac{1}{2}(1 - 3m_3^2) \times \left[\frac{3I_7(\beta,\gamma)}{2I_8(\beta,\gamma)} - \frac{1}{2}\right] = \frac{1}{2}(1 - 3m_3^2)\Phi(\beta,\gamma) \quad (29)$$

The reduced dichroism for β and γ is

$$\left(\frac{A_\parallel - A_\perp}{A^0}\right)_{\beta,\gamma} = \left(\frac{\Delta\epsilon}{\epsilon}\right)_{\beta,\gamma} = \frac{3}{2}(3m_3^2 - 1) \times \left[\frac{3I_7(\beta,\gamma)}{2I_8[\beta,\gamma)} - \frac{1}{2}\right] = \frac{3}{2}(3m_3^2 - 1)\Phi(\beta,\gamma) \quad (30)$$

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[33] Some indications of this behavior were obtained in dichroism measurements of very high molecular weight samples of polybutylisocyanates: unpublished observations of J. B. Milstein and E. Charney.

$\Phi(\beta,\gamma)$, which is defined by eq 11, is a quantity loosely called the degree of orientation or the orientation function or factor, the properties of which have been thoroughly examined by previous workers.[20,21] The experimentally observed dichroism is then the product of the optical transition moment and the orientation function.

In order to study the direction of the transition moments in a chromophore, it is now necessary to separate these two quantities. If the field dependence of the electric dichrosim is studied up to sufficiently high electric fields, a simple extrapolation to the saturating field should, in principle, yield the desired quantity, $m_3{}^2$, since $\Phi(\beta,\gamma > 0) \rightarrow 1$ and $\Phi(\beta,\gamma < 0) \rightarrow -{}^1/_2$ as $E \rightarrow \infty$. In combination with eq 18 the reduced dichroism at a given electric field strength can be written as eq 31 (provided that $\Delta\mu_i$ and $\Delta\alpha_{ii}$ are both nearly zero); for $\gamma > 0$ and $\gamma < 0$. This expression can be used to analyze the experimental curves of the reduced dichroism obtained at various field strengths so that the contribution of the permanent dipole moment can be compared with that of the electric polarizability anisotropy in the electronic ground state. It should be noted that the low field reduced dichroism apparently becomes zero if $\beta^2 + 2\gamma = 0$ for negative values of γ and that for this case eq 31 is not applicable. A detailed account of the method of separating β and γ has already been given for electric birefringence data of synthetic polyamino acids.[31]

$$\frac{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,\gamma}}{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\ll 1}} = \frac{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,\gamma}}{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,|\gamma|\ll 1}} = \frac{15\Phi(\beta,\gamma)}{\beta^2 + 2\gamma} \quad (31)$$

For sufficiently strong electric field strengths the expressions corresponding to eq 31 will be written as eq 32 for $\gamma > 0$, and for $\gamma < 0$ and $\beta/2|\gamma| < 1$ in eq 33. At saturating fields, the terms in β and/or γ become zero in which case the resulting simpler expressions may be used to evaluate $\Phi(\beta,\gamma)$ if the corresponding data are available.

$$\frac{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,\gamma}}{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,\gamma\gg 1}} = \frac{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,\gamma}}{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,\gamma\gg 1}} = \frac{\Phi(\beta,\gamma)}{1 - \dfrac{2}{\beta + 2\gamma}} \quad (32)$$

$$\frac{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,\gamma}}{\left(\dfrac{A_\parallel - A_\perp}{A^0}\right)_{\beta,|\gamma|\gg 1}} = \frac{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,\gamma}}{\left(\dfrac{\Delta\epsilon}{\epsilon}\right)_{\beta,|\gamma|\gg 1}} = -\frac{2\Phi(\beta,\gamma)}{1 + \dfrac{3}{2\gamma}} \quad (33)$$

Once the orientation factor is estimated the component of the transition moment along the symmetry axis, $m_3{}^2$, can be determined. Thus, the sign of the electric dichroism is positive, zero, or negative when the angle θ ($\cos^2\theta = m_3{}^2$) between the transition moment and the symmetry axis is smaller, equal to, or larger than $\theta - 54.735°$ or $3\cos^2\theta - 1 = 0$. This situation is very much like that in electric birefringence where a similar relationship exists between the transition moment direction and the symmetry axis.[34] In addition, from $\Phi(\beta,\gamma)$ thus evaluated at various field strengths E, it is now possible to obtain the magnitude of the ground state permanent electric dipole moment along the symmetry axis, μ_3, and the magnitude and sign of the ground state electric polarizability anisotropy ($\alpha_{33} - \alpha_{11}$).

B. Electric Dichroism Involving Both Electronic Ground and Excited States. When the electrooptical properties of an excited state differ appreciably from those of the electronic ground state, the effect of electrochromism should be noticeable. The use of the term electrochromism appears to be due to Platt,[1] who first considered the effect of an external electric field upon the shift of the color of conjugated organic dyes in solution. Electrochromism may be defined simply as the difference between absorbance of unpolarized monochromatic light in the presence, A^E, and that in the absence, A^0, of the electric field applied perpendicular to the direction of progagation of light through an absorbing medium. With use of polarized light electrochromism may also be measured by setting the plane of polarization at an angle of 54.735° with respect to the direction of the electric field, or by summing the individually measured parallel and perpendicular dichroism (see eq 17); since the relation $A^E = (A_\parallel + 2A_\perp)/3$ holds identically, eq 34 shows that these three methods are all able to determine the effect of electrochromism experimentally.

$$\frac{A^E - A^0}{A^0} = \frac{A_{54.7°}{}^E - A^0}{A^0} = \frac{1}{3}\left(\frac{A_\parallel + 2A_\perp}{A^0}\right) - 1 \quad (34)$$

At low electric field electrochromism depends on the square of the field strength (eq 19). The permanent dipole moment term in the first member is dependent on temperature, whereas the electric polarizability difference between ground and excited state is not. Hence it would be possible to separate the $\mu_3\Delta\mu_3$ term from the $\Sigma\Delta\alpha_{ii}$ term and once the ground state dipole moment μ_3 is available independently, $\Delta\mu_3$ may be obtained. On the other hand, at saturating fields the electrochromism becomes independent of temperature for both models (eq 23 and 26). For prolate ellipsoids, however, the $\Delta\mu_3$ term is now linear with respect to the field strength, while the $\Delta\alpha_{33}$ term depends on the square of the strength. Thus, the measurement of electrochromism as a function of field strength may yield information with regard to the relative magnitude of $\Delta\alpha_{33}$ and ($\Delta\alpha_{11} + \Delta\alpha_{22}$), and the contribution of ($\Delta\mu_1{}^2 + \Delta\mu_2{}^2$) to the sum of permanent dipole moment differences, $\Sigma\Delta\mu_i{}^2$. It would also be possible to specify the molecular shape by comparing eq 23 and 26, since for oblate ellipsoids the electrochromism at saturating fields is dependent only on the square of the electric field strength.

Appendix

Case A. Polarizability Orientation ($\beta = 0, \gamma \neq 0$). Prolate and Oblate Ellipsoid Models. (1) At low fields ($|\gamma| \ll 1$) for both prolate ($\gamma > 0$) and oblate ($\gamma < 0$)

$$\frac{I_7}{I_8} = \frac{1}{3}\left(1 + \frac{4}{15}\gamma + \frac{8}{315}\gamma^2 + \ldots\right)$$

$$\frac{I_3}{I_8} = \frac{1}{5}\left(1 + \frac{8}{21}\gamma + \frac{16}{315}\gamma^2 + \ldots\right)$$

$$\frac{I_9}{I_8} = \frac{I_5}{I_8} = 0$$

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[34] E. Charney and R. S. Halford, *J. Chem. Phys.*, 29, 221 (1958).

(2) At high fields ($|\gamma| \gg 1$) for prolate ($\gamma > 0$)

$$\frac{I_7}{I_8} = 1 - \frac{1}{\gamma} - \frac{1}{2\gamma_2} - \dots$$

$$\cong 1 - \frac{2}{2\gamma - 1}$$

$$\frac{I_3}{I_8} = 1 - \frac{2}{\gamma} - \dots$$

$$\cong 1 - \frac{4}{2\gamma - 1}$$

and for oblate ($\gamma < 0$, $\beta/2|\gamma| < 1$)

$$\frac{I_7}{I_8} \cong -\frac{1}{2\gamma} - \dots$$

$$\frac{I_3}{I_8} \cong \frac{3}{4\gamma^2} - \dots$$

(3) At arbitrary fields (any β or γ), for prolate ($\gamma > 0$)

$$\frac{I_7}{I_8} = \frac{1}{2}\left[\frac{e^{\gamma}}{\sqrt{\gamma}I(\sqrt{\gamma})} - \frac{1}{\gamma}\right]$$

$$\frac{I_3}{I_8} = \frac{3}{4\gamma^2} + \left(1 - \frac{3}{2\gamma}\right)\frac{e^{\gamma}}{2\sqrt{\gamma}I(\sqrt{\gamma})}$$

where

$$I(\sqrt{\gamma}) \equiv \int_0^{\sqrt{\gamma}} e^{x^2}\mathrm{d}x$$

and for oblate ($\gamma < 0$)

$$\frac{I_7}{I_8} = \frac{1}{\gamma}\left[\frac{\sqrt{-\frac{\gamma}{\pi}}e^{\gamma}}{\mathrm{erf}(\sqrt{-\gamma})} - \frac{1}{2}\right]$$

$$\frac{I_3}{I_8} = \frac{1}{\gamma}\left[\frac{3}{4\gamma} + \left(1 - \frac{3}{2\gamma}\right)\frac{\sqrt{-\frac{\gamma}{\pi}}e^{\gamma}}{\mathrm{erf}(\sqrt{-\gamma})}\right]$$

where

$$\mathrm{erf}(\sqrt{-\gamma}) \equiv \frac{2}{\sqrt{\pi}}\int_0^{\sqrt{-\gamma}} e^{-x^2}\mathrm{d}x$$

Case B. Permanent Dipole Orientation ($\beta \neq 0, \gamma = 0$). Sphere and Unpolarizable Models Only. (1) At low fields ($\beta \ll 1$)

$$\frac{I_9}{I_8} = \frac{\beta}{3} - \frac{\beta^3}{45} + \frac{2\beta^5}{945} - \dots$$

$$\frac{I_7}{I_8} = \frac{1}{3} + \frac{2\beta^3}{45} - \frac{4\beta^4}{945} + \dots$$

$$\frac{I_5}{I_8} = \frac{\beta}{5} - \frac{\beta^3}{105} + \dots$$

$$\frac{I_3}{I_8} = \frac{1}{5} + \frac{4\beta^2}{105} + \dots$$

(2) At high fields ($\beta \gg 1$)

$$\frac{I_9}{I_8} = 1 - \frac{1}{\beta} + \dots$$

$$\frac{I_7}{I_8} = 1 - \frac{2}{\beta} + \frac{2}{\beta^2} - \dots$$

$$\frac{I_5}{I_8} = 1 - \frac{3}{\beta} + \frac{6}{\beta^2} - \dots$$

$$\frac{I_3}{I_8} = 1 - \frac{4}{\beta} + \frac{12}{\beta^2} - \dots$$

(3) At arbitrary fields (any β)

$$\frac{I_9}{I_8} = \coth\beta - \frac{1}{\beta}$$

$$\frac{I_7}{I_8} = 1 + \frac{2}{\beta^2} - \frac{2}{\beta}\coth\beta$$

$$\frac{I_5}{I_8} = \left(1 + \frac{6}{\beta^2}\right)\coth\beta - \frac{3}{\beta}\left(1 + \frac{2}{\beta^2}\right)$$

$$\frac{I_3}{I_8} = \left(1 + \frac{12}{\beta^2} + \frac{24}{\beta^3}\right) - \frac{4}{\beta}\left(1 + \frac{6}{\beta^2}\right)\coth\beta$$

Case C. Dipole-Polarizability Mixed Orientation ($\beta \neq 0, \gamma \neq 0$). Prolate and Oblate Ellipsoid Models. (1) At low fields ($\beta \ll 1$, $|\gamma| \ll 1$), for both prolate ($\gamma > 0$) and oblate ($\gamma < 0$)

$$\frac{I_9}{I_8} = \frac{\beta}{3} + \frac{4\beta\gamma}{45} - \frac{\beta^3}{45} - \frac{16\beta^3\gamma}{945} + \frac{8\beta\gamma^2}{954} + \frac{2\beta^5}{945} \dots$$

$$\frac{I_7}{I_8} = \frac{1}{3} + \frac{2\beta^2}{45} + \frac{4\gamma}{45} - \frac{4\beta^4}{945} + \frac{8\gamma^2}{945} + \frac{8\beta^2\gamma}{945} \dots$$

$$\frac{I_5}{I_8} = \frac{\beta}{5} - \frac{\beta^3}{105} + \frac{8\beta\gamma}{105} - \frac{16\beta^3\gamma}{945} + \frac{2\beta^5}{945} + \dots$$

$$\frac{I_3}{I_8} = \frac{1}{5} + \frac{4\beta^2}{105} + \frac{8\gamma}{105} + \frac{8\gamma^2}{945} - \frac{4\beta^4}{945} \dots$$

(2) At high fields ($\beta \gg 1, |\gamma| \gg 1$) prolate ($\gamma > 0$)

$$\frac{I_9}{I_8} = 1 - \frac{1}{\beta} + \frac{2\gamma}{\beta^2} + \dots$$

$$\cong 1 - \frac{1}{\beta + 2\gamma}$$

$$\frac{I_7}{I_8} = 1 - \frac{2}{\beta} + \frac{4\gamma}{\beta^2} \dots$$

$$\cong 1 - \frac{2}{\beta + 2\gamma}$$

$$\frac{I_5}{I_8} = 1 - \frac{3}{\beta} + \frac{6\gamma}{\beta^2} + \dots$$

$$\cong 1 - \frac{3}{\beta + 2\gamma}$$

$$\frac{I_3}{I_8} = 1 - \frac{4}{\beta} + \frac{8\gamma}{\beta^2} + \dots$$

$$\cong 1 - \frac{4}{\beta + 2\gamma}$$

and for oblate ($\gamma < 0$, $\beta/2|\gamma| < 1$)

$$\frac{I_9}{I_8} = -\frac{\beta}{2\gamma} + \dots$$

$$\frac{I_7}{I_8} = \frac{\beta^2}{4\gamma^2} - \frac{\beta}{2\gamma} + \dots$$

$$\frac{I_5}{I_8} = \frac{3\beta}{4\gamma^2} - \left(\frac{\beta}{2\gamma}\right)^3 + \dots$$

$$\frac{I_3}{I_8} = \frac{3}{4\gamma^2} - \frac{3\beta^2}{4\gamma^3} + \frac{\beta^4}{16\gamma^4} + \dots$$

(3) At arbitrary fields (any β and γ), for both prolate ($\gamma > 0$) and oblate ($\gamma < 0$)

$$\frac{I_9}{I_8} = \frac{e^{\gamma}}{\gamma I_8}\sinh\beta - \frac{\beta}{2\gamma}$$

$$\frac{I_7}{I_8} = \frac{e^{\gamma}}{\gamma I_8}\left[\cosh\beta - \frac{\beta}{2\gamma}\sinh\beta\right] + \left(\frac{\beta}{2\gamma}\right)^2 - \frac{1}{2\gamma}$$

$$\frac{I_5}{I_8} = \left(1 - \frac{1}{\gamma}\right)\frac{I_9}{I_8} + \frac{\beta}{2\gamma}\left(1 - \frac{I_7}{I_8}\right),$$

$$\frac{I_3}{I_8} = \frac{\beta}{2\gamma^2}\frac{I_9}{I_8} + \frac{1}{2\gamma}\left(1 - \frac{\beta^2}{2\gamma}\right) + \left(1 - \frac{3}{2\gamma} + \frac{\beta^2}{4\gamma^2}\right)\frac{I_7}{I_8}$$

where I_8 is given by eq 23 for $\gamma > 0$ and by eq 24 for $\gamma < 0$

On the Shapes and Energetics of Polyatomic Molecules[1,2]

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Abstract: A model is presented for the prediction of shapes and energetics of the low-lying electronic states of small polyatomic molecules. Molecules are considered which have one or two central atoms and which involve coordination numbers two or three. The following assumptions are made. (1) *Simple valence bond structures are adequate to describe the bonding.* (2) *Structures with completed shells on terminal atoms are preferred. Between alternative such structures, the one for which all atoms are neutral is preferred.* (3) *Crude models of these localized structures can be used to determine molecular shapes with classical electrostatics.* (4) *The proper disposition of lone pairs on central atoms is obtained by using the crystal field theory to describe the interaction between them and the closed shells on terminal atoms.* The qualitative ideas and predictions largely conform with those of Pauling, Walsh, Gillespie, and others. Successful quantitative predictions are made of many bond angles and bending force constants for excited as well as ground states and several barriers to internal rotation. The use of an electrostatic model is justified from the polyatomic virial theorem, and a method of localizing canonical self-consistent-field molecular orbitals is proposed which brings conventional molecular orbital theory into coincidence with the model.

In the 1930's it became clear that the *number* of valence electrons determines the shapes of small polyatomic molecules.[4] In 1952, Walsh gave the first unified explanation of this essential chemical fact.[5] His arguments were a comprehensive modification, extension, and reinterpretation of the molecular orbital approach introduced by Mulliken for AB_2 molecules.[6] In addition to rationalizing the shapes of a great variety of molecules in their ground states, Walsh gave a detailed discussion of the spectra of the molecules and of their excited-state geometries. His work has enormously aided the interpretation and analysis of molecular electronic spectra; it is a triumph of the molecular orbital method.

Comprehensive discussions of geometry have also been given in terms of localized descriptions of the bonding. The valence-shell electron pair repulsion theory (VSEPR) gives a good description of the ground states of a great many molecules by focusing on the effects of repulsions between lone pair and bonding electrons.[4c,7] The classical valence bond theory (VB) concentrates on the nature of the hybridization at central atoms.[8] With both of these methods, the geometry of a molecule can be rationalized *if* an appropriate localized description is displayed. They both suffer from not providing a clear way to decide between alternative localized pictures. Also, neither method gives a satisfactory way of interpreting the observed electronic spectra or explaining the geometry in excited states.

Since we will be using concepts in our discussion which have been clearly stated in one or more of these earlier discussions, it is important to identify these at the outset. Our considerable indebtedness to earlier authors should then be clear throughout the rest of our analysis.

Both the VB and the VSEPR theories have demonstrated that *simple localized pictures are adequate to describe geometry.* In both theories, the role of lone pair electrons on central atoms is of paramount importance in fixing geometry. Walsh's MO discussion can be rigorously transformed into a localized picture in which central-atom lone pairs are emphasized. Indeed, Walsh gave a very explicit discussion of the bending process which is equivalent to that which we will give.[9] Walsh stated the assumptions underlying his

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(2) Based on part of a thesis submitted by Gary W. Schnuelle in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University, 1972.

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