OPTICAL ANISOTROPIES OF MOLECULES

I. THEORY OF OPTICAL ROTATORY POWER
II. KERR EFFECT APPLIED TO CONFORMATIONAL ANALYSIS

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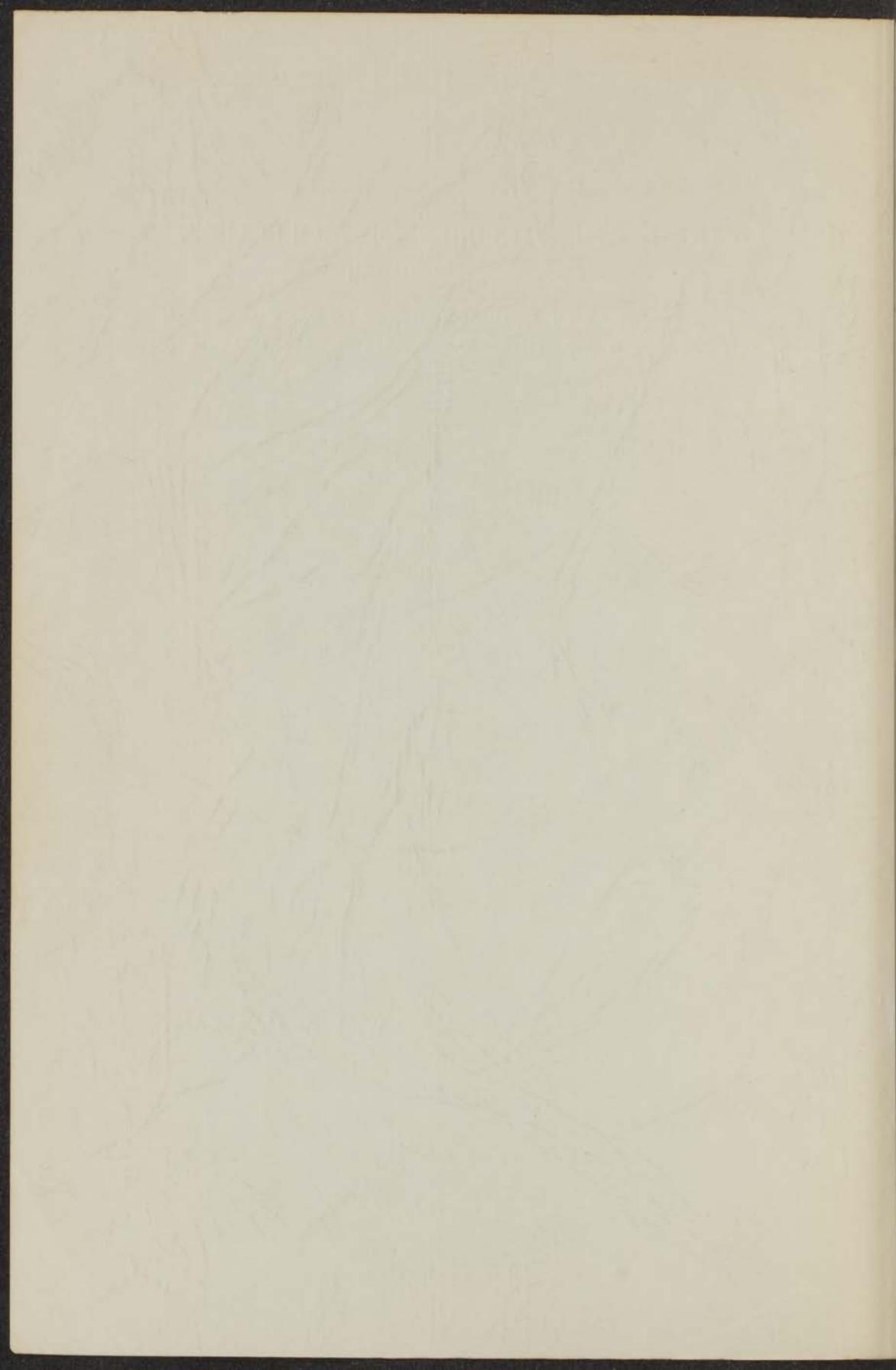
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PROEFSCHRIFT

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WILLEM JOHANNES ALBERT MAASKANT
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Aan mijn ouders

Aan mijn vrouw

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INTRODUCTION

One of the most versatile methods of obtaining information about the dynamics of electrons and nuclei in molecules is the study of their interaction with electromagnetic radiation. Two aspects are especially important in this respect:
1. Energy exchange between molecule and radiation.
2. Polarization of the molecule and the associated scattering of light.

If radiation energy is absorbed or emitted, the frequency of the electromagnetic field at which it occurs is directly proportional to energy differences between stationary states. The intensity of these processes are determined by electric or magnetic transition moments. Both quantities (energy differences and transition moments) are very helpful in testing theoretical deductions about the structure of the molecules.

Very often absorption or emission occurs outside the region that is accessible with current laboratory equipment. It then becomes worth-while to study the polarization of the molecules, induced by the electromagnetic radiation and vibrating with the same frequency. This can be done - in principle - at all frequencies. Therefore it could constitute a more convenient method of investigation, but unfortunately the interpretation in terms of molecular structure is less direct than in the case of an absorption or emission spectrum.

In principle a complete knowledge of all the absorption bands contains the same information as the knowledge of a complete dispersion curve of the polarizability, since both effects are closely related (Kramers-Kronig relations). In practice, however, usually a small region of the spectrum is only accessible. Then experimental conditions determine the choice of the quantity to be studied.

In this thesis we will only be concerned with polarizabilities. In practice one does not study the polarizabilities of a single molecule, but the response to a beam of light of a large number of molecules which compose a piece of matter. In reality one mea-

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sures the refractive index or the rotation of the plane of pola-
rization. Therefore the problem arises how these phenomenological
quantities can be used to derive the constants which characterize
an isolated molecule.

The classical solution to this problem due to Lorentz (1880)
and Lorenz (1881) leads to the formula[*]):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} \nu \alpha_o$$

where n is the refractive index, ν is the number of particles in
1 cc. and α_o is the mean polarizability of a molecule.

In organic chemistry the molar refraction:

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d_o}$$

where M is the molecular weight and d_o the density of the sub-
stance, has some time played an important role as an aid in de-
termining structural formulae. At present the average polarizabi-
lity of a molecule, on which the molar refraction depends, does
not contribute much to the deepening of our insight. Much more
important is the study of the anisotropy of the polarizability,
which reveals itself in birefringence, and the investigation of
higher order polarizabilities, which are responsible for the phe-
nomenon of optical rotatory power. In this thesis two aspects of
polarizability will be studied. First we will deal with the rela-
tions of the rotatory power of a piece of matter and the molecu-
lar third order polarizabilities, characteristic of a single mo-
lecule. In the second place we report the application of electric
birefringence to the determination of the structure of some orga-
nic molecules.

[*]) Throughout the first part of this thesis we use rationalized
gaussian units.

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PART ONE

THEORY OF OPTICAL ROTATORY POWER

PART. ONE

THEORY OF OPTICAL ROTATORY POWER

CHAPTER 1

FORMULATION OF THE PROBLEM

General considerations

If a plane-polarized beam of light traverses a piece of optically active transparant matter the rotation of the plane of polarization is related to a difference in refractive index of right- and left-handed circularly polarized light. The relation is expressed in the equation:

$$\chi = \frac{\pi}{\lambda_{vac}} (n_- - n_+)$$

1.1

Here χ is the angle in radians/cm over which the plane of polarization has rotated, n_- and n_+ are the refractive indices for left- and right-handed circularly polarized light and λ_{vac} is the wave length of the light in vacuo. The problem is to relate the phenomenological quantities n_- and n_+ to molecular constants.

In the theory of electrons the phenomenological quantities that appear in the Maxwell equations, and that characterize the propagation of light in matter, arise through an averaging procedure, which eliminates the rapid variations which occur on a molecular scale. Therefore one has to explain the contribution of a molecule to these averages in terms of its intrinsic properties and of its interaction with other molecules.

Each molecule which is perturbed by an electromagnetic field becomes itself the source of secondary radiation. Thus the field polarizing a molecule is built up by the primary field coming from outside the matter and the fields scattered by all the other molecules. Therefore the first question with which one is confronted in the development of the theory is:
1. How is the averaged field perturbing a single molecule - called the local field - related to macroscopic quantities?

The primary as well as the secondary radiation propagates with the velocity of light in vacuo c. The averaged quantities, however, describe waves which travel through matter with a smaller velocity c/n. A second question which has to be answered is:

2. What is the detailed mechanism by which the incident wave is eliminated and is replaced by a wave with a different velocity?

The solution to this problem is known as the extinction theorem.

The problems 1 and 2 are dealt with in chapters 3 and 4. Before, in chapter 2, we will discuss the response of a single molecule to an electromagnetic perturbation.

Historical remarks

The response of an optically active molecule to a beam of light was formulated quantummechanically by Rosenfeld (1928). More special but still rather general models are due to Condon et al. (1937) (one-electron model) and to Kooy (1936) and Kirkwood (1937) (a system of coupled oscillators).

A large number of papers have appeared dealing with the problem of the local field. In Lorentz' model (1915, 1952) the correlations of a molecule with its neighbours do not appear explicitly. Kirkwood (1936) and Yvon (1937, II) were the first to take account of the correlation in position, Kirkwood in a theory on the static dielectric constant, Yvon also in a theory on refraction. Böttcher (1952) corrected the Clausius-Mosotti and the Lorentz-Lorenz equation by using Onsager's concept of the reaction field, which also involves a correlation effect. In a series of papers by Jansen, Mandel and Mazur (1955, 1956) the ideas introduced by Kirkwood and Yvon were combined with the effect derived by Jansen and Mazur about the dependence of the polarizability on the density of the gas. In a theory of the electric birefringence Mazur and Postma (1959) also included the correlation in orientation of the molecules.

In all these theories the dimension of the molecules was considered to be negligible with respect to the wavelength of the light, so that the local field could be regarded as constant over a molecule. In the theory of optical rotatory power variations of the local field inside the molecule have to be known. The calculation of the variation of the local field gives rise to specific difficulties and has led to several controversial statements about the influence of the refractive index on the rotation. Primarily Born (1918) derived that the rotation was proportional to a factor $\left(\dfrac{n^2 + 2}{3}\right)^2$. Later (1933) he changed this factor in $\left(\dfrac{n^2 + 2}{3}\right)$. The first result was also reached by Kooy (1936), while de Malleman (1924, 1925) proposed a factor 1. Finally Hoek (1939) gave a very thorough discussion in which he analysed the origin of the discrepancies.

The extinction theorem is due to Ewald (1912, 1916) and Oseen (1915). A somewhat different approach was given by Darwin (1924) who considered a plane parallel slab of matter. A general derivation of the theorem applied to normal refraction as well as opti-

cal activity and applicable to a piece of matter of unspecified
form was described by Hoek (1939, 1941). Postma (1959) reformula-
ted this theorem for birefringent media. In other treatises
(e.g. Yvon) the extinction theorem is not mentioned, but is im-
plicitly accepted by using Maxwell's equations.

Although the problems of the local field and the extinction
theorem were treated very satisfactorily by Hoek, the incorpora-
tion of the correlation effects is lacking. In particular for the
optical rotatory power these effects should not be neglected.
Goossens (1958) attempted to approach the problem by applying On-
sager's reaction field, but it remains uncertain whether the in-
fluence of correlations on optical activity is thereby satisfac-
torily accounted for. It is our aim to give a treatment which
allows for the explicit introduction of correlation effects in
the calculation of the internal derivatives of the field. We will
restrict ourselves, however, to the case in which the molecular
polarizabilities can be considered as independent from the mole-
cular environment. We therefore exclude any change due to the
formation of e.g. hydrogen-bonds and charge-transfer complexes,
or due to local electrostatic fields, or the presence of other
polarizable molecules (Jansen-Mazur effect).

CHAPTER 2

RESPONSE OF AN ISOLATED MOLECULE TO A LIGHT WAVE

Introduction

In the theory of dispersion usually the semiclassical method is used (Kramers[*], 1938, Chapter 8). This method consists in calculating by quantummechanical theory the current distribution in the molecules induced by a light wave, whereas the electromagnetic field remains unquantized. This current distribution is then supposed to behave as a classical source of scattered radiation. Where, in this chapter we collect the ingredients necessary for the statistical treatment of the rotatory dispersion problem we can therefore as far as radiation is concerned restrict ourselves to the classical formulae (A). Correspondingly the response of a molecule is first described with classical polarizability tensors (B), which are further explained quantummechanically in Section C.

A. Classical radiation formulae

The microscopic Maxwell-Lorentz equations, which describe the electromagnetic fields and their dependences on the charge and current distribution are:

$$c \nabla \times \underline{e} + \underline{\dot{h}} = 0 \qquad\qquad 2.1$$

$$c \nabla \times \underline{h} - \underline{\dot{e}} = \rho \underline{v} \qquad\qquad 2.2$$

$$\nabla \cdot \underline{h} = 0 \qquad\qquad 2.3$$

$$\nabla \cdot \underline{e} = \rho \qquad\qquad 2.4$$

[*]) Abbreviated in this thesis by Kr.

e and h are the microscopic electric and magnetic fieldstrengths respectively, ρ is the charge density and v is the charge velocity, consequently ρv is the current density. The equation of continuity follows from 2.2 and 2.4:

$$\nabla \cdot (\rho v) + \dot{\rho} = 0 \qquad 2.5$$

The fieldstrengths can be derived from a scalar potential $\bar{\phi}$ and a vector potential a:

$$e = - \nabla \bar{\phi} - \frac{1}{c} \dot{a} \qquad 2.6$$

$$h = \nabla \times a \qquad 2.7$$

$\bar{\phi}$ and a are not completely defined by these equations. Their choice can be restricted by the so-called Lorentz gauge:

$$\nabla \cdot a + \frac{1}{c} \dot{\bar{\phi}} = 0 \qquad 2.8$$

Consequently $\bar{\phi}$ and a satisfy the wave equations:

$$\Delta \bar{\phi} - \frac{1}{c^2} \ddot{\bar{\phi}} = -\rho \qquad 2.9$$

$$\Delta a - \frac{1}{c^2} \ddot{a} = - \frac{(\rho v)}{c} \qquad 2.10$$

Solutions of these equations are:

$$\bar{\phi}_A = \int_V \frac{\{\rho\}_B}{4\pi r_{AB}} dV_B \qquad 2.11$$

$$a_A = \frac{1}{c} \int_V \frac{\{\rho v\}_B}{4\pi r_{AB}} dV_B \qquad 2.12$$

to which solutions of the homogeneous equations can be added. r_{AB} is the distance between two points A and B and the braces

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mean that ρ and $\rho \underline{v}$ have to be taken at the retarded time $(t - r_{AB}/c)$. For normal refraction and optical rotation only those components of ρ and $\rho \underline{v}$ are of importance, which are induced by the light wave and which have the same time dependency. The same applies to other field quantities and they can therefore be written as the product of a time independent part and a factor $e^{i \omega t}$, where ω is the circular vibration frequency of the light.

By virtue of 2.5 it is possible to derive the charge and current density from a single vector.

$$\rho \underline{v} = \dot{\underline{p}}' \qquad \rho = - \underline{\nabla} \cdot \underline{p}' \qquad\qquad 2.13$$

$\underline{p}' = \dfrac{1}{i\omega} \rho \underline{v}$ is the dipole moment density of the - microscopic - true charge distribution.

Similarly $\tilde{\phi}$ and $\underline{a}$ can be derived from a Hertz potential $\underline{z}$:

$$\underline{a} = \dfrac{1}{c} \dot{\underline{z}} \qquad \tilde{\phi} = - \underline{\nabla} \cdot \underline{z} \qquad\qquad 2.14$$

$\underline{z} = \dfrac{c}{i\omega} \underline{a}$ satisfies the wave equation:

$$\Delta \underline{z} - \dfrac{1}{c^2} \ddot{\underline{z}} = -\underline{p}' \qquad\qquad 2.15$$

The solution of this equation is:

$$\underline{z}_A = \int\limits_V \dfrac{\{\underline{p}'\}_B}{4 \pi r_{AB}} dV_B \quad \text{or} \quad \underline{z}_A = \int\limits_V \underline{p}'_B \dfrac{e^{-i k r_{AB}}}{4 \pi r_{AB}} dV_B \qquad\qquad 2.16$$

to which solutions of the homogeneous equation can be added and where $\underline{e}$ and $\underline{h}$ can be derived from $\underline{z}$ by:

$$\underline{e} = \underline{\nabla} \underline{\nabla} \cdot \underline{z} - \dfrac{1}{c^2} \ddot{\underline{z}} \qquad\qquad 2.17$$

$$\underline{h} = \dfrac{1}{c} \underline{\nabla} \times \dot{\underline{z}} \qquad\qquad 2.18$$

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Since all quantities depend on time by a factor $e^{i\omega t}$, we can simplify these equations to:

$$\underline{e} = \nabla\nabla \cdot \underline{z} + k^2\underline{z} \qquad\qquad 2.19$$

$$\underline{h} = ik\nabla \times \underline{z} \qquad\qquad 2.20$$

When the dipole moment distribution of a scattering molecule is known, the Hertz potential can be determined by eq. 2.16. If the molecules are spherical or nearly spherical it is useful to enclose the entire source by the smallest possible sphere and to develop the dipole distribution with respect to the centre of this sphere. The Hertz vector outside this sphere can then be developed in a series consisting of products of spherical Bessel- and Hankelfunctions, and Legendre polynomials (Stratton, 1941; Phillips, 1962) or in terms of so-called "irreducible tensors" (cf. Rose, 1957).

Darwin (1924) and Hoek (1939, 1941) use a Taylor series development which can be written as:

$$\underline{z}_A = \int_V \underline{p}'_B \, e^{\underline{r}_B \cdot \nabla} \, \frac{e^{-ikR_A}}{4\pi R_A} \, dV_B \qquad\qquad 2.21$$

R_A is the distance of A to the molecular centre. $\underline{r}_B$ is the vector from this origin to some point B in the molecule. The nabla operator differentiates the function of R_A at the molecular centre. The integration is over the molecular volume.

When we take only the first two terms of the series and in addition assume that the wavelength of light is much larger than the radius of the molecular sphere, both developments are identical.

The result is[*]):

$$\underline{z}_A = \underline{p}\,\frac{e^{-ikR_A}}{4\pi R_A} + \underline{q} \cdot \nabla\,\frac{e^{-ikR_A}}{4\pi R_A} \qquad\qquad 2.22$$

where $\underline{p} = \int_V \underline{p}'_B \, dV_B$ and $\underline{q} = \int_V \underline{p}'_B \, \underline{r}_B \, dV_B$ $\qquad\qquad 2.23$

[*]) For the vector and tensor notation see p. 56.

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In index notation:

$$(z_A)_\alpha = P_\alpha \frac{e^{-ikR_A}}{4\pi R_A} + q_{\alpha\beta} \nabla_\beta \frac{e^{-ikR_A}}{4\pi R_A} \qquad 2.24$$

For later use we give the formula of the electric field, arising from eq. 2.19 and 2.22:

$$\underline{e} = (\nabla\nabla + k^2 \underline{U}) \cdot \left\{ \underline{p} \frac{e^{-ikR_A}}{4\pi R_A} + \underline{q} \cdot \nabla \frac{e^{-ikR_A}}{4\pi R_A} \right\} \qquad 2.25$$

or $\quad e_\alpha = (\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta}) \left\{ p_\beta \frac{e^{-ikR_A}}{4\pi R_A} + q_{\beta\gamma} \nabla_\gamma \frac{e^{-ikR_A}}{4\pi R_A} \right\} \qquad 2.26$

Here $\underline{U}$ or $U_{\alpha\beta}$ is the second order unit tensor. The first term between the braces gives the electric dipole radiation. The second term is responsible for magnetic dipole and quadrupole radiation (See e.g. Jeffreys and Jeffreys 1956, section 24.23).
Not all redundancy is avoided in these formulae since the Hertz vector may contain a part which corresponds to a zero electric field (See p. 25).

B. I n t r o d u c t i o n   o f   m o l e c u l a r   p o l a -
      r i z a b i l i t y   t e n s o r s

The dipole moment distribution p' which according to the previous section determines the radiation field, depends itself on the electric field distribution inside the molecule originating from outside the molecule.

$$\underline{p}'(\underline{x}) = \int_{mol} \underline{\underline{\sigma}}(\underline{x},\underline{x}') \cdot \underline{e}(\underline{x}') \, d\underline{x}' \qquad 2.27$$

The polarizability $\underline{\underline{\sigma}}(\underline{x},\underline{x}')$ is a second order tensor density, which relates the fieldstrength at the point $\underline{x}'$ to the polariza-

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tion at $\underline{x}$. The quantity $\underline{\sigma}(\underline{x}, \underline{x}')$ is a generalization of the tensors $\underline{A}^{kl}$ introduced by Born in his theory of optical rotatory power (Born, Optik, p. 406). Born considers a molecule consisting of a number of coupled anisotropic harmonic oscillators. $\underline{A}^{kl}$ gives the dependence of the polarization of oscillator k from the electric fieldstrength at oscillator l. In Born's theory the fundamental relation

$$A_{\alpha\beta}^{kl} = A_{\beta\alpha}^{lk} \qquad\qquad 2.28$$

was derived on the assumption that the coupled oscillators form a conservative system. It will be shown in the next section that a similar relation exists for the tensor density $\underline{\sigma}(\underline{x}, \underline{x}')$:

$$\sigma_{\alpha\beta}(\underline{x}, \underline{x}') = \sigma_{\beta\alpha}(\underline{x}', \underline{x}) \qquad\qquad 2.29$$

$\underline{\sigma}(\underline{x}, \underline{x}')$ is not only a generalization of Born's model in the sense that a continuous distribution of oscillators is considered, but also encompasses the one-electron model introduced by Condon et al. (1937). It then describes how the induced motion of the electron at point $\underline{x}$ depends on the fieldstrength everywhere inside the molecule.

It is advantageous to characterize the state of polarization of a molecule with the moments of the continuous dipole distribution since for our purpose a few moments suffice (See e.g. eq. 2.25). On the other hand for the dependence of these moments on the electric field distribution it will be sufficient to develop the electric field by a Taylor expansion with respect to the origin and to restrict ourselves to the first two terms. We write:

$$\underline{e}(\underline{x}') = e^{(\underline{x}' \cdot \underline{\nabla})} \underline{e} \qquad\qquad 2.30$$

where the differentiations are to be taken at the centre of the molecule.

The total dipole moment of the molecule is:

$$\underline{p} = \int \underline{p}'(\underline{x}) \, d\underline{x} = \underline{p}^{(1)} + \underline{p}^{(2)} + \ldots\ldots \qquad\qquad 2.31$$

where:

$$\underline{p}^{(1)} = \iint \underline{\sigma}(\underline{x}, \underline{x}') \, d\underline{x} \, d\underline{x}' \cdot \underline{e} = \underline{\alpha} \cdot \underline{e} \qquad\qquad 2.32$$

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and:

$$p^{(2)} = \iint \underline{\sigma}(\underline{x}, \underline{x}') \ \underline{x}' \ d\underline{x} \ d\underline{x}' \ : \ (\nabla \underline{e}) = \underline{\underline{\beta}} : (\nabla \underline{e}) \qquad 2.33$$

The second moment is defined by:

$$q = \int \underline{p}'(\underline{x})\underline{x} \ d\underline{x} = \iint \underline{\sigma}(\underline{x}, \underline{x}')\underline{x} \ d\underline{x} \ d\underline{x}' \cdot \underline{e} = \underline{\underline{\beta}}' \cdot \underline{e} \qquad 2.34$$

In the case of the second moment we will retain the first term of the expansion. For the sake of clarity we will describe the equations 2.32, 2.33 and 2.34 also in index notation:

$$p_\alpha^{(1)} = \iint \sigma_{\alpha\beta}(\underline{x}, \underline{x}')d\underline{x} \ d\underline{x}' \ e_\beta = \alpha_{\alpha\beta} \ e_\beta \qquad 2.35$$

$$p_\alpha^{(2)} = \iint \sigma_{\alpha\beta}(\underline{x}, \underline{x}')x_\gamma' \ d\underline{x} \ d\underline{x}' \ (\nabla_\gamma e_\beta) = \beta_{\alpha\beta\gamma}(\nabla_\gamma e_\beta) \qquad 2.36$$

$$q_{\alpha\gamma} = \iint \sigma_{\alpha\beta}(\underline{x}, \underline{x}')x_\gamma \ d\underline{x} \ d\underline{x}' \ e_\beta = \beta_{\alpha\beta\gamma}' \ e_\beta \qquad 2.37$$

C. Quantummechanical derivation of the polarizability tensors

As mentioned in the introduction to this chapter the calculation of the current density distribution which determines the Rayleigh scattering of a molecule in a stationary state n is essentially a quantummechanical problem with the solution (Kr. eq. 8-223)[*]:

$$\left[\rho\underline{v}\right]_{nn} = \frac{1}{c} \ \underline{W} \qquad 2.38$$

where:

$$\underline{W} = \sum_m{}' \left\{ \frac{\{\rho\underline{v}^\circ\}_{nm} \int \underline{a} \cdot \{\rho\underline{v}^\circ\}_{mn} \ dV}{\hbar(-\omega + \omega_{mn})} + \right.$$

$$\left. + \frac{(\int \underline{a} \cdot \{\rho\underline{v}^\circ\}_{nm} \ dV)\{\rho\underline{v}^\circ\}_{mn}}{\hbar(\omega + \omega_{mn})} - \underline{a} \ \zeta_{nn} \right\} \qquad 2.39$$

[*] Kramers explicitly indicates that the real part of the righthand side has to be taken. In the present considerations it will not be confusing to omit this indication.

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The dash beside the summation sign denotes that $m \neq n$. $\underline{a}$ is the microscopic vector potential inside the molecular volume, coming from outside the molecule. ω and ω_{mn} are the circular frequency of the incident light and the circular transition frequency from $m \to n$ ($\hbar \omega_{mn} = E_m - E_n$). $\{\rho \underline{v}^{\circ}\}_{mn}$ is the matrix element of the unperturbed current density operator, which is given by (cf. Kr. eq. 8-9):

$$\{\rho \underline{v}^{\circ}\}_{nm} = \sum_i \left[\int \frac{1}{2} (\phi_n^* \, e_i \, \underline{v}_i^{\circ} \, \phi_m + \phi_m \, e_i \, \underline{v}_i^{\circ*} \, \phi_n^*) \prod_{\substack{j \\ j \neq i}} d\underline{x}_j \right]_{\underline{x}_i = \underline{x}} \qquad 2.40$$

ϕ_n and ϕ_m are time independent wavefunctions.
The unperturbed velocity operator is:

$$\underline{v}_i^{\circ} = \frac{1}{m_i} (\underline{p}_i)_{\text{op}} \quad (\text{Kr. eq. 8-4}) \qquad 2.41$$

Here $(\underline{p}_i)_{\text{op}}$ is the momentum operator of particle i, m_i is its mass.

$$\zeta_{nn} = \sum_i \frac{e_i^2}{m_i} \left[\int \phi_n^* \, \phi_n \prod_{\substack{j \\ j \neq i}} d\underline{x}_j \right]_{\underline{x}_i = \underline{x}} \qquad (\text{Kr. eq. 8-221}) \qquad 2.42$$

The current distribution $[\rho \underline{v}]_{nn}$ depends on time through $\underline{a}$ which contains the timefactor $e^{i\omega t}$, therefore:

$$\underline{p}' = \frac{1}{i\omega c} \underline{W} \qquad 2.43$$

Since $\underline{a}$ is the vector potential of the field which has its origin outside the molecule it behaves as a field in vacuo. This implies that it is possible to choose the gauge of the potentials $\bar{\phi}$ and $\underline{a}$ such that $\bar{\phi} = 0$.
Consequently:

$$\underline{\nabla} \cdot \underline{a} = 0 \qquad 2.44$$

and

$$\underline{e} = -\frac{1}{c} \dot{\underline{a}} \qquad 2.45$$

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Combining 2.39, 2.43 and 2.45:

$$\underline{p}' = \frac{1}{\omega^2} \underline{W}' \qquad \qquad 2.46$$

where

$$\underline{W}' = \Sigma' _m \left\{ \frac{\{\rho\underline{v}^\circ\}_{nm} \int \underline{e} \cdot \{\rho\underline{v}^\circ\}_{mn} \, dV}{\hbar(-\omega + \omega_{mn})} + \right.$$

$$\left. + \frac{(\int \underline{e} \cdot \{\rho\underline{v}^\circ\}_{nm} \, dV)\{\rho\underline{v}^\circ\}_{mn}}{\hbar(\omega + \omega_{mn})} - \zeta_{nn} \, \underline{e} \right\} \qquad 2.47$$

This can be written as:

$$\underline{p}'(\underline{x}) = \int \underline{\eta}(\underline{x},\underline{x}') \cdot \underline{e}(\underline{x}')d\underline{x}' + \zeta(\underline{x}) \, \underline{e}(\underline{x}) \qquad 2.48$$

where $\underline{x}$ and $\underline{x}'$ are the coordinates of two points within the molecule.

$$\eta_{\alpha\beta}(\underline{x},\underline{x}') = \frac{1}{\omega^2} \Sigma' _m \left\{ \frac{\{\rho v^\circ_\alpha(\underline{x})\}_{nm} \, \{\rho v^\circ_\beta(\underline{x}')\}_{mn}}{\hbar(-\omega + \omega_{mn})} + \right.$$

$$\left. + \frac{\{\rho v^\circ_\beta(\underline{x}')\}_{nm} \, \{\rho v^\circ_\alpha(\underline{x})\}_{mn}}{\hbar(\omega + \omega_{mn})} \right\} \qquad 2.49$$

$$\zeta(\underline{x}) = -\frac{1}{\omega^2} \zeta_{nn} \qquad \qquad 2.50$$

Comparing 2.48 with 2.27 it appears that η and ζ together are equivalent to $\underline{\sigma}(\underline{x},\underline{x}')$:

$$\underline{\sigma}(\underline{x},\underline{x}') = \underline{\eta}(\underline{x},\underline{x}') + \zeta(\underline{x}) \, \delta(\underline{x} - \underline{x}')\underline{U} \qquad 2.51$$

$\delta(\underline{x} - \underline{x}')$ is the Dirac δ-function. $\underline{U}$ is a second order unit tensor. $\underline{\eta}(\underline{x},\underline{x}')$ as well as $\zeta(\underline{x})$ are real quantities. This can easily be shown by choosing all the wavefunctions φ_n, φ_m real, which is always possible if the Hamilton operator, having ϕ_n and ϕ_m as eigenfunctions, does not contain an imaginary part.

$\{\rho\underline{v}^\circ\}_{nm}$ is then an imaginary operator and from 2.40 it is clear that:

$$\{\rho\underline{v}^\circ\}_{nm} = -\{\rho\underline{v}^\circ\}_{nm}^* = -\{\rho\underline{v}^\circ\}_{mn} \qquad 2.52$$

Eq. 2.49 can be simplified now to:

$$\eta_{\alpha\beta}(\underline{x},\underline{x}') = \frac{2}{\omega^2}\sum_m{}' \omega_{mn} \frac{\{\rho v_\alpha^\circ(\underline{x})\}_{nm}\ \{\rho v_\beta^\circ(\underline{x}')\}_{mn}}{\hbar(\omega_{mn}^2 - \omega^2)} \qquad 2.53$$

It follows from this equation that:

$$\eta_{\alpha\beta}(\underline{x},\underline{x}') = \eta_{\beta\alpha}(\underline{x}',\underline{x}) \qquad 2.54$$

Since $\zeta\underline{U}$ is isotropic a similar formula applies to $\underline{\sigma}(\underline{x},\underline{x}')$:

$$\sigma_{\alpha\beta}(\underline{x},\underline{x}') = \sigma_{\beta\alpha}(\underline{x}',\underline{x}) \qquad 2.55$$

which was already mentioned before.

For the general formulae for $\underline{\alpha}$, $\underline{\beta}$ and $\underline{\beta}'$ we have to substitute in 2.32, 2.33 and 2.34 the expression for $\underline{\sigma}(\underline{x},\underline{x}')$. The results are:

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_m{}' \frac{\omega_{mn}}{\omega_{mn}^2 - \omega^2} (P_{nm})_\alpha\ (P_{mn})_\beta \qquad 2.56$$

$$\beta_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_m{}' \frac{1}{\omega_{mn}^2 - \omega^2} \frac{1}{\omega_{mn}} \int\{\rho v_\alpha^\circ(\underline{x})\}_{nm}\ d\underline{x} \int \{\rho v_\beta^\circ(\underline{x}')\}_{mn}\ x'_\gamma\ d\underline{x}' \qquad 2.57$$

$$\beta'_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_m{}' \frac{1}{\omega_{mn}^2 - \omega^2} \frac{1}{\omega_{mn}} \int\{\rho v_\alpha^\circ(\underline{x})\}_{nm}\ x_\gamma d\underline{x} \int \{\rho v_\beta^\circ(\underline{x}')\}_{mn}\ d\underline{x}' \qquad 2.58$$

Here

$$P_{nm} = \frac{1}{i\,\omega_{nm}}\dot{P}_{nm} = \frac{1}{i\,\omega_{nm}}\int\{\rho\underline{v}^\circ(\underline{x})\}_{nm}\ d\underline{x} \quad \text{(Kr. eq. 8-24)} \qquad 2.59$$

For the derivation of the well-known formula 2.56 use is made of:

$$\frac{1}{i\hbar}\sum_m \left[(P_{nm})_\alpha\ (\dot{P}_{mn})_\beta - (\dot{P}_{nm})_\beta\ (P_{mn})_\alpha\right] = \sum_i \frac{e_i^2}{m_i}U_{\alpha\beta} \qquad 2.60$$

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which are the commutation relations of $\underline{P}_{nm}$ and $\dot{\underline{P}}_{nm}$ (Kr. eq. 8-204).
Similarly for the derivation of $\underline{\beta}$ and $\underline{\beta}'$ use is made of the
analogous relations:

$$\frac{1}{i\hbar} \sum_m \left[(P_{nm})_\alpha \int \{\rho v_\beta^\circ(\underline{x}')\}_{mn} x_\gamma' d\underline{x}' - \int \{\rho v_\beta^\circ(\underline{x}')\}_{nm} x_\gamma' d\underline{x}' (P_{mn})_\alpha \right] =$$

$$= \sum_i \frac{e_i^2}{m_i} (x_\gamma)_{nn} U_{\alpha\beta} \qquad\qquad 2.61$$

D. General remarks

I. Magnetic dipole and electric quadrupole moment

A number of authors prefer to formulate the response of a
single molecule to an electromagnetic perturbation in terms of
electric and magnetic moments. This has an advantage if one
assumes that the phenomenological quantities $\underline{P}$ and $\underline{M}$ which occur
in the equations:

$$\underline{D} = \underline{E} + \underline{P} \qquad\qquad 2.62$$

$$\underline{B} = \underline{H} + \underline{M} \qquad\qquad 2.63$$

depend on the molecular moments in a well-known way, so that this
relation offers no problem (e.g. Rosenfeld (1928), Condon et al.
(1937), Eyring et al. (1949)). Since we do not start with the
assumption that the dependence of $\underline{P}$ and $\underline{M}$ from molecular mo-
ments is known beforehand - in fact we even do not need this
dependency - it is not necessary to introduce magnetic moments as
such.

For the sake of comparison, however, we will give the relation
between the second order moment q and the usual definitions of
magnetic and quadrupole moments.

The magnetic moment is defined by:

$$\underline{m} = \frac{1}{2c} \int_V \underline{x} \times (\rho \underline{v}) d\underline{x} \qquad\qquad 2.64$$

(Heitler, 1954, p. 24, eq. 23b)

with 2.13, 2.34 and 2.37:

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$$m_\alpha = \frac{1}{2c} [\alpha\beta\gamma] \dot{q}_{\gamma\beta} = \frac{1}{2c} [\alpha\beta\gamma] \beta'_{\gamma\epsilon\beta} \dot{e}_\epsilon \qquad 2.65$$

where $[\alpha\beta\gamma]$ is the permutation tensor.

$[\alpha\beta\gamma] = 1$ for $\alpha = 1$, $\beta = 2$, $\gamma = 3$ or cycl.

$[\alpha\beta\gamma] = -1$ for $\alpha = 2$, $\beta = 1$, $\gamma = 3$ or cycl.

$[\alpha\beta\gamma] = 0$ for $\alpha = \beta$, $\beta = \gamma$ or $\gamma = \alpha$

The quadrupole moment can be defined by the equation:

$$k_{\alpha\gamma} = \int_V p'_\alpha\, x_\gamma d\underline{x} + \int_V p'_\gamma\, x_\alpha d\underline{x} \qquad 2.66$$

(Stratton, 1941, p. 433, eq. 17)

Consequently:

$$k_{\alpha\gamma} = q_{\alpha\gamma} + q_{\gamma\alpha} \qquad 2.67$$

Generally the quadrupole moment is neglected in considerations about optical rotatory power, as its influence vanishes for an isotropic liquid if the molecules have no specific interaction (See chapter 5, eq. 5.4). Vol'kenshtein (1950) showed that for anisotropic media the quadrupole moment can not be neglected because of the conservation of energy. In the case of an isotropic liquid where the molecules can have a strong interaction we cannot neglect them either.

II. Duplicate rule

Since $\underline{\nabla} \cdot \underline{e} = 0$ we can add to $\beta_{\alpha11}$, $\beta_{\alpha22}$ and $\beta_{\alpha33}$ an arbitrary vector component σ_α, without changing the dipole moment. A similar relation holds for the tensor $\underline{\beta}'$. Here the reason is that the Hertz vector may contain a part which corresponds to zero electric field (See p. 18). This implies that:

$$\beta'_{1\beta1} + \beta'_{2\beta2} + \beta'_{3\beta3} = \text{arbitrary} \qquad 2.68$$

(cf. Hoek, thesis, p. 52)

Similar relations also apply to higher order polarizability tensors. (Darwin's duplicate rule, Darwin, 1924).

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CHAPTER 3

THE AVERAGE QUANTITIES

Introduction

The response of a single molecule to a monochromatic light wave, which was discussed in the former chapter, forms the basis of the study of a system of many molecules. The first task is to set up equations which give the polarization of an arbitrarily selected molecule due to the primary field and the secondary fields of all the other molecules. These equations have to be averaged in order to obtain macroscopic quantities (section A). In the reduction of these equations we make use of molecular distribution functions (section B) and the closely related distinction between short-range and long-range interactions (section C). In section D the macroscopic polarizability densities are derived.

A. Fundamental equations

We consider a medium consisting of N equivalent molecules in statistical equilibrium. These molecules are supposed to be sufficiently spherical so that the series development of the Hertz vector discussed in the preceding chapter (eq. 2.21) can be applied. The position of a molecule is specified by the coordinates of its centre and by its orientation, both with respect to a space-fixed coordinate system. The polarizabilities $\underline{\alpha}$, $\underline{\beta}$ and $\underline{\beta}'$, which were introduced in chapter 2B, are so defined that the determination of the polarization of a molecule requires only the knowledge of the effective electric field and its derivative at the molecular centre.

The electric field to which a molecule k is subjected consists of the primary field $\underline{E}^e$ coming from outside the medium and the secondary fields scattered by all the other molecules. This is expressed in the formula:

$$e(\underline{R}) = \underline{E}^e(\underline{R}) - \sum_l{}' \underline{F}(\underline{R},\underline{R}_l) \cdot \underline{p}_l - \sum_l{}' \underline{H}(\underline{R},\underline{R}_l) : \underline{q}_l \qquad 3.1$$

or

$$e_\alpha(\underline{R}) = E^e_\alpha(\underline{R}) - \sum_l{}' F_{\alpha\beta}(\underline{R},\underline{R}_l) \cdot p^{(l)}_\beta - \sum_l{}' H_{\alpha\beta\gamma}(\underline{R},\underline{R}_l) : q^{(l)}_{\beta\gamma} \qquad 3.2$$

The dash at the Σ sign means that $l = k$ has to be omitted.

$$F_{\alpha\beta}(\underline{R},\underline{R}_l) = -(\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta})\,\frac{e^{-ik\left|\underline{R}_l - \underline{R}\right|}}{4\pi \left|\underline{R}_l - \underline{R}\right|} \qquad 3.3$$

$$H_{\alpha\beta\gamma}(\underline{R},\underline{R}_l) = -(\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta}) \nabla_\gamma \frac{e^{-ik\left|\underline{R}_l - \underline{R}\right|}}{4\pi \left|\underline{R}_l - \underline{R}\right|} \qquad 3.4$$

$\underline{R}$ is the position vector in a space-fixed coordinate system of a point inside molecule k; $\underline{R}_l$ denotes the centre of the molecule l. The differentiations are applied at $\underline{R}_l$. These formulae follow immediately from 2.25.

The polarization moments of molecule k can be calculated from the electric field and its derivative by:

$$\underline{p} = \underline{p}^{(1)} + \underline{p}^{(2)} = \underline{\alpha} \cdot \underline{e}(\underline{R}_k) + \underline{\beta} : (\nabla \underline{e})_{\underline{R}=\underline{R}_k} \qquad 3.5$$

$$\underline{q} = \underline{\beta}' \cdot \underline{e}(\underline{R}_k) \qquad 3.6$$

From these equations it follows that:

$$\underline{p}_k = \underline{\alpha}_k \cdot \underline{E}^e_k - \sum_l{}' \underline{\alpha}_k \cdot \underline{F}_{kl} \cdot \underline{p}_l - \sum_l{}' \underline{\alpha}_k \cdot \underline{H}_{kl} : \underline{q}_l$$

$$+ \underline{\beta}_k : \left\{ (\nabla \underline{E}^e)_k - \sum_l{}' (\nabla \underline{F}_{kl}) \cdot \underline{p}_l \right\} \qquad 3.7$$

$$\underline{q}_k = \underline{\beta}'_k \cdot \underline{E}^e_k - \sum_l{}' \underline{\beta}'_k \cdot \underline{F}_{kl} \cdot \underline{p}_l \qquad 3.8$$

Products of third order polarizabilities are neglected, since their contribution to the dipole moment of k is small with respect to other terms. Therefore the moments $\underline{q}_l$ do not appear in

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the expression for the derivative of the electric field (eq. 3.7).
Similarly the moments q_l are neglected in eq. 3.8.

It is from these equations that expressions for the macroscopic
moment densities as statistical averages have to be derived. Via
the Maxwell equations these macroscopic moment densities determi-
ne the propagation of light through the medium.

The averaging procedure may be formulated in different ways.
Kirkwood (1936), Yvon (1937) and also Mazur et al. (1955, 1956,
1959) use ensemble averages, whereas Hoek (1939, 1941) and Rosen-
feld (1951), following Lorentz (1902), think in terms of space
averages. This approach has the advantage of a certain visualiza-
tion, especially if the liquid for which the laws of light
refraction are derived is actually a rigid glass. We prefer,
following Kramers (1938, § 95), to consider our averages as
"averages over planes of constant light phase". Since in the
theory of optical rotatory power the dimensions of a molecule can
no longer be neglected with respect to the wave length of light,
the volume over which an average has to be taken should be small
compared to a molecular diameter, at least in the direction of
the light wave. Therefore the volume element has to be inclosed
by two planes of constant light phase, a very small distant apart,
but of sufficient extension to contain a large number of mole-
cules. A molecule is considered to be inside the volume element
if its centre is. For the rest the averaging procedure is
identical to that described by Hoek (1939, p. 25) and Rosenfeld
(1951, chapter VI, § 1).

Indicating average values by a bar, eq. 3.7 becomes:

$$\overline{\underline{p}_k} = \overline{\underline{\alpha}_k} \cdot \underline{E}_k^e - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{F}_{kl}} \cdot \underline{p}_l - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{H}_{kl}} : \underline{q}_l$$

$$+ \overline{\underline{\beta}_k} : (\underline{\nabla} \underline{E}^e)_k - \sum_l{}' \overline{\underline{\beta}_k : \underline{\nabla}_k \underline{F}_{kl}} \cdot \underline{p}_l \qquad 3.9$$

The bar means that the average is extended over the positions of
the centres and orientations of all the molecules, except over
the position of the centre of molecule k. $\overline{\underline{p}_k}$, $\overline{\underline{\alpha}_k}$ thus become
functions of $\underline{R}_k$. The averaging is actually performed by inte-
gration of eq. 3.7 after multiplication by an appropriate distri-
bution function. This function gives the relative frequency
density of finding all the molecules with their centres at spe-
cified points and with given orientations. In the neighbourhood

of molecule k the distribution of the centres and orientations of molecules l will strongly depend on the position and orientation of k. At greater distances this correlation gradually disappears. There it is allowed to average over the positions and orientations of molecules l disregarding the position and orientation of k.

Let us assume for a moment that everywhere correlations between molecules can be neglected. If then as an example we consider the second term of eq. 3.9, it becomes:

$$-\sum_l{}' \overline{\underline{\alpha}_k} \cdot \underline{F}_{kl} \cdot \overline{\underline{p}_l} \qquad\qquad 3.10$$

The bar over $\underline{F}_{kl}$ has to be continued as a second bar over $\overline{\underline{p}_l}$, because $\overline{\underline{p}_l}$ still depends on the position of the centre of l.

This expression suggests the introduction of the internal field and the internal derivative of the field:

$$\underline{E}_k^w = \underline{E}_k^e - \sum_l{}' \overline{\underline{F}_{kl} \cdot \overline{\underline{p}_l}} - \sum_l{}' \overline{\underline{H}_{kl} : \overline{\underline{q}_l}} \qquad\qquad 3.11$$

and

$$(\underline{\nabla}\underline{E})_k^w = (\underline{\nabla}\underline{E}^e)_k - \sum_l{}' \overline{(\underline{\nabla}_k\underline{F}_{kl}) \cdot \overline{\underline{p}_l}} \qquad\qquad 3.12$$

In 3.12 a term with $\underline{q}$ has been omitted. With these expressions 3.9 can be written as:

$$\overline{\underline{p}_k} = \overline{\underline{\alpha}_k} \cdot \underline{E}_k^w + \overline{\underline{\beta}_k} : (\underline{\nabla}\underline{E})_k^w$$

$$- \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{F}_{kl} \cdot \underline{p}_l} - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{H}_{kl} : \underline{q}_l} - \sum_l{}' \overline{\underline{\beta}_k : \underline{\nabla}_k\underline{F}_{kl} \cdot \underline{p}_l}$$

$$+ \sum_l{}' \overline{\underline{\alpha}_k} \cdot \overline{\underline{F}_{kl} \cdot \overline{\underline{p}_l}} + \sum_l{}' \overline{\underline{\alpha}_k} \cdot \overline{\underline{H}_{kl} : \overline{\underline{q}_l}} + \sum_l{}' \overline{\underline{\beta}_k} : \overline{\underline{\nabla}_k\underline{F}_{kl} \cdot \overline{\underline{p}_l}} \qquad 3.13$$

In the same way we find for 3.8:

$$\overline{\underline{q}_k} = \overline{\underline{\beta}_k'} \cdot \underline{E}_k^w - \sum_l{}' \overline{\underline{\beta}_k' \cdot \underline{F}_{kl} \cdot \underline{p}_l} + \sum_l{}' \overline{\underline{\beta}_k'} \cdot \overline{\underline{F}_{kl} \cdot \overline{\underline{p}_l}} \qquad 3.14$$

When all correlations are neglected $\overline{\underline{p}_k}$ becomes:

$$\overline{\underline{p}_k} = \overline{\underline{\alpha}_k} \cdot \underline{E}_k^w + \overline{\underline{\beta}_k} : (\underline{\nabla}\underline{E})_k^w \qquad\qquad 3.15$$

and

$$\overline{\underline{q}_k} = \overline{\underline{\beta}_k'} \cdot \underline{E}_k^w \qquad\qquad 3.16$$

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3.15 and 3.16 form together the simplest approximations for the moments of an optically active molecule.

B. Molecular distribution functions

A further reduction of the equations 3.13 and 3.14 can be obtained with the molecular distribution functions introduced by Kirkwood (1936) and Yvon (1937) and generalized to include orientations by Mazur and Postma (1959). These functions can be derived from a general distribution function, which for a system in equilibrium and neglecting velocity dependent effects can be written as:

$$f = C \exp\{- U_o(\underline{R}_N, \theta_N)/\kappa T\} \qquad 3.17$$

Here κ is Boltzmann's constant and $U_o(\underline{R}_N, \theta_N)$ is the intermolecular energy dependent on the coordinates and orientations of all the molecules. C is a normalization constant determined by:

$$<f> = 1 \qquad 3.18$$

where in the usual way brackets indicate integration over all variables.

In view of the further reduction of equations 3.13 and 3.14 we summarize the definitions and properties of the simplest molecular distribution functions.

The number density is defined by:

$$\nu(\underline{R}) = \sum_{i=1}^{N} <\delta(\underline{R}_i - \underline{R})f> \qquad 3.19$$

Similarly:

$$n_1(\underline{R}, \theta) = \sum_{i=1}^{N} <\delta(\underline{R}_i - \underline{R}) \, \delta(\theta_i - \theta)f> \qquad 3.20$$

$n_1(\underline{R}, \theta)$ is the density of molecules with position $\underline{R}$ and orientation θ. In a homogeneous medium both $\nu(\underline{R})$ and $n_1(\underline{R}, \theta)$ are uniform - except close to the boundary of the system - and therefore in fact independent of $\underline{R}$. The molecular distribution functions pertaining simultaneously to pairs of molecules are:

$$n_2(\underline{R},\underline{R}') = \sum_{i,j=1}^{N}{}' \langle \delta(\underline{R}_i - \underline{R})\delta(\underline{R}_j - \underline{R}')f \rangle \qquad 3.21$$

$$n_2(\underline{R},\underline{R}',\theta,\theta') = \sum_{i,j=1}^{N}{}' \langle \delta(\underline{R}_i - \underline{R})\delta(\underline{R}_j - \underline{R}')\delta(\theta_i - \theta)\delta(\theta_j - \theta')f \rangle \quad 3.22$$

In a homogeneous and isotropic medium $n_2(\underline{R},\underline{R}')$ and $n_2(\underline{R},\underline{R}',\theta,\theta')$ depend on $\underline{R}$ and $\underline{R}'$ only through the distance $R_{12} = |\underline{R}' - \underline{R}|$. For $n_2(\underline{R},\underline{R}')$ Yvon derived a power series in $1/N$:

$$n_2(\underline{R},\underline{R}') = \nu^2\{g(R_{12}) + \frac{1}{N} h(R_{12}) + \dots\} \qquad 3.23$$

For increasing R_{12}:

$$g(R_{12}) \longrightarrow 1 \quad \text{and} \quad h(R_{12}) \longrightarrow h_o(R_{12}) \qquad 3.24$$

(cf. Yvon (1937, I, p. 25, eq. 67), F. Brown (1956, p. 65, 66))

Like $n_2(\underline{R},\underline{R}')$, $n_2(\underline{R},\underline{R}',\theta,\theta')$ and similar distribution functions for three or more particles tend to products of distribution functions of a smaller number of molecules when the intermolecular distances increase. Yvon showed that in liquids and gases consisting of molecules which are small with respect to the wave length of light, the influence of the correlation between molecules is restricted to an area, which is also small compared to the wave length. In addition Yvon proved that the reaction field which still would exist if mechanical correlations could be disregarded is due to interactions which are also restricted to a region of the same extension. We assume with Mazur and Postma (1959) that these results also apply for the orientational part of the correlations.

In view of these considerations it is expedient to introduce the concept of a "correlation sphere" with a radius of the same order of magnitude as the "correlation length". The idea is that the molecule which is at the centre of this sphere feels the influence of the molecules outside the sphere as if they form a continuum. The molecules inside the sphere, however, have to be considered as particles.

C. Long-range and short-range interactions

With the aid of the molecular distribution functions the

formulae for the internal field and the internal derivative of the field can be written as:

$$\underline{E}^w(\underline{R}) = \underline{E}^e(\underline{R}) - \nu^{-2} \int \underline{F}(\underline{R},\underline{R}') n_2(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}') d\underline{R}'$$

$$- \nu^{-2} \int \underline{H}(\underline{R},\underline{R}') n_2(\underline{R},\underline{R}') : \underline{Q}(\underline{R}') d\underline{R}' \qquad 3.25$$

$$(\underline{\nabla}\underline{E})^w(\underline{R}) = (\underline{\nabla}\underline{E}^e)(\underline{R}) - \nu^{-2} \int \underline{\nabla}_R \underline{F}(\underline{R},\underline{R}') n_2(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}') d\underline{R}' \qquad 3.26$$

where the macroscopic polarization densities are defined by:

$$\underline{P}(\underline{R}) = \nu \underline{p}_k \qquad 3.27$$

$$\underline{Q}(\underline{R}) = \nu \underline{q}_k \qquad 3.28$$

The integrals over $\underline{R}'$ can be applied to the whole medium, since the distribution function $n_2(\underline{R},\underline{R}')$ becomes zero for distances $|\underline{R}' - \underline{R}|$ smaller than a molecular diameter and therefore singularities do not occur. Actually, however, a sphere with its centre at $\underline{R}$ can be excluded from the integral without changing its value as long as its radius is small with respect to the wave length of light. This result which was already known in the theory of the normal refraction also applies to optically active systems, as is shown in the appendix. The derivation depends essentially on the properties of $\underline{F}(\underline{R},\underline{R}')$ for small values of the argument $|\underline{R}' - \underline{R}|$ and the assumption that the variations of $\underline{P}$ over a region of the order of magnitude of the correlation sphere are comparable to the variations of the primary field.

We will choose the correlation sphere as the volume to be excluded from the integrations since outside this sphere $n_2(\underline{R},\underline{R}') = \nu^2$ (except to terms proportional to $1/N$, which will be neglected). 3.25 and 3.26 become:

$$\underline{E}^w(\underline{R}) = \underline{E}^e(\underline{R}) + \underline{E}^d(\underline{R}) \qquad 3.29$$

where:

$$\underline{E}^d(\underline{R}) = - \int\limits_{o(R)}^{V} \underline{F}(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}') d\underline{R}' - \int\limits_{o(R)}^{V} \underline{H}(\underline{R},\underline{R}') : \underline{Q}(\underline{R}') d\underline{R}' \qquad 3.30$$

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$$(\nabla \underline{E})^w(\underline{R}) = (\nabla \underline{E}^e)(\underline{R}) - \int_{o(R)}^{V} \nabla_R \underline{F}(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}')d\underline{R}' \qquad 3.31$$

Because the correlations between k and l vanish outside the correlation sphere, the terms in the second and third row of 3.13 pertaining to molecules in that region cancel. The same applies to the second and third term in 3.14.

The assumption that the correlation radius is small with respect to the wave length implies that the $\underline{F}_{kl}$-operator for the particles inside the correlation sphere can be replaced by the static dipole-dipole tensor $\underline{T}_{kl}$.

$$\underline{T}_{kl} = \nabla\nabla \frac{1}{4\pi r_{lk}} \qquad 3.32$$

Yvon showed this approximation to be valid in the theory of normal refraction. In the case of optical activity it cannot be adopted without further inquiry. However, the validity still holds since the terms in the series development of $\underline{F}_{kl}$ after $\underline{T}_{kl}$ contain k to the second and higher powers. For similar reasons $\underline{H}_{kl} \longrightarrow \nabla_l \underline{T}_{kl}$. (See appendix).

In the appendix it is also shown that $\overline{\underline{T}_{kl}} = 0$, $\overline{\nabla_l \ \underline{T}_{kl}} = 0$, $\overline{\underline{T}_{kl} \ r_{lk}} = 0$ and $\overline{\nabla_l \ \underline{T}_{kl} \ r_{lk}} = 0$. Therefore the third row of 3.13 and the third term in 3.14 are zero. Thus we reach the results:

$$\overline{\underline{P}_k} = \overline{\underline{\alpha}_k} \cdot \underline{E}_k^w + \overline{\underline{\beta}_k} : (\nabla \underline{E})_k^w - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{P}_l}$$

$$- \sum_l{}' \overline{\underline{\alpha}_k \cdot \nabla_l \underline{T}_{kl}} : \underline{q}_l - \sum_l{}' \overline{\underline{\beta}_k : \nabla_k \underline{T}_{kl} \cdot \underline{P}_l} \qquad 3.33$$

and

$$\overline{\underline{q}_k} = \overline{\underline{\beta}_k'} \cdot \underline{E}_k^w - \sum_l{}' \overline{\underline{\beta}_k' \cdot \underline{T}_{kl} \cdot \underline{P}_l} \qquad 3.34$$

The summations over l, now only refer to molecules inside the correlation sphere.

Apparently the electric field at particle k is composed of three contributions:

a. The primary field $\underline{E}^e$.

b. The field due to the polarization outside the correlation

sphere, which can be calculated as arising from a continuum, $\underline{E}^d$ (3.30).

c. The short-range contribution due to the granular structure of the medium inside the correlation sphere.

The derivative of the field can be divided similarly.

As will be shown in the next chapter, the field arising from the continuum can be written as the sum of two surface integrals: one over the surface of the correlation sphere, the other over the external surface. This last integral cancels the primary field (extinction theorem). A consequence of this situation is that the electric field at molecule k can be calculated from contributions arising from the immediate neighbourhood of molecule k only.

D. The macroscopic polarization densities

In order to evaluate 3.33 and 3.34, which after multiplication with ν give the macroscopic polarization densities $\underline{P}$ and $\underline{Q}$, we have to substitute expressions for $\underline{p}_l$ and $\underline{q}_l$. For the moments of a molecule l we will not use expressions similar to 3.33 and 3.34, but instead we will try to write the polarizing field at l in terms of $\underline{E}_k^w$ and $(\underline{\nabla}\underline{E})_k^w$. In a certain sense we could say that the field coming into the correlation sphere from outside is regarded as a "primary" field for all molecules which are inside this sphere. This "primary" field is supposed to be described sufficiently accurately by:

$$\underline{E}_k^w + \underline{r}_{lk} \cdot (\underline{\nabla}\underline{E})_k^w \qquad\qquad 3.35$$

where $\underline{r}_{lk}$ is the vector pointing from the centre of k to the centre of l. This field differs from the field which actually polarizes molecule l according equations similar to 3.33 and 3.34. The difference is due to the neglect of correlations between molecules l inside the correlation sphere and outside. But the idea of the correlation sphere is that these correlations are not perceivable at molecule k and thus are of no importance for the calculation of $\overline{\underline{p}_k}$.

Up to terms quadratic in the polarizabilities 3.33 becomes:

$$\overline{p}_k = \overline{\underline{\alpha}_k} \cdot \underline{E}_k^w + \overline{\underline{\beta}_k} : (\underline{\nabla}\underline{E})_k^w - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l} \cdot \underline{E}_k^w$$

$$- \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} : \underline{\beta}_l'} \cdot \underline{E}_k^w$$

$$- \sum_l{}' \overline{\underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \cdot \underline{\alpha}_l} \cdot \underline{E}_k^w$$

$$- \sum_l{}' \overline{(\underline{\alpha}_k \cdot \underline{T}_{kl} \underline{r}_{lk} \cdot \underline{\alpha}_l)} : (\underline{\nabla}\underline{E})_k^w$$

$$- \sum_l{}' \overline{(\underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} \underline{r}_{lk} : \underline{\beta}_l')} : (\underline{\nabla}\underline{E})_k^w$$

$$- \sum_l{}' \overline{(\underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \underline{r}_{lk} \cdot \underline{\alpha}_l)} : (\underline{\nabla}\underline{E})_k^w$$

$$- \sum_l{}' \overline{\underline{\alpha}_l \cdot \underline{T}_{kl} \cdot \underline{\beta}_l} : (\underline{\nabla}\underline{E})_k^w$$

$$+ \sum_{l,m}{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lm} \cdot \underline{p}_m} + \sum_{l,m}{}' \overline{\underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} : \underline{\beta}_l' \cdot \underline{T}_{lm} \cdot \underline{p}_m}$$

$$+ \sum_{l,m}{}' \overline{\underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lm} \cdot \underline{p}_m} + \sum_{l,m}{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\beta}_l : \underline{\nabla}_l \underline{T}_{lm} \cdot \underline{p}_m}$$

$$+ \sum_{l,m}{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{\nabla}_m \underline{T}_{lm} : \underline{q}_m} \qquad \text{3.36}$$

This series can be continued to any desired accuracy. In the last
five terms we have omitted for the sake of brevity to substitute
the appropriate expressions for p_m and q_m. We will need these
terms later in a discussion of the reaction field. The success of
this development depends on how many terms have to be taken into
account.

The terms quadratic in the polarizability will be discussed in
some detail. In the third column the terms $- \sum_l{}' \underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} : \underline{\beta}_l' \cdot \underline{E}_k^w$
and $- \sum_l{}' \underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{E}_k^w$ are corrections to the first term
$- \sum_l{}' \underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{E}_k^w$. These corrections arise if it is deemed
worth-while to account of third order polarizabilities. The ratio
of these correction terms to the principal term is about equal to a
molecular radius divided by the intermolecular distance. They are
as important in the theory of the static dielectric constant as
in the theory of refraction. Nevertheless they are almost always
neglected. The terms of the last column, proportional to the
internal derivative of the field, are responsible for optical
activity. The first is the counterpart of a molecular model of
coupled oscillators as are encountered in the theories of Born
(1933), Kuhn (1932), Kooy (1936) and Kirkwood (1937). The other
three are again correction terms, which are smaller than the

first by the same previously mentioned ratio. Since for dense media this factor is not very small (it can amount to 0.3) it may be worth-while to investigate numerically the influence of the contributions of polarizabilities, of higher order than the third.

Similar remarks apply to the expression for the moment $\overline{q}_k$ which follows from 3.34:

$$\overline{q}_k = \overline{\underline{\beta}'_k \cdot \underline{E}^w_k} - \sum_l{}' \overline{\underline{\beta}'_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l} \cdot \underline{E}^w_k - \sum_l{}' \overline{(\underline{\beta}'_k \cdot \underline{T}_{kl} \underline{r}_{lk} \cdot \underline{\alpha}_l)} : (\underline{\nabla E})^w_k$$

$$+ \sum_{l,m}{}' \overline{\underline{\beta}'_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lm} \cdot \underline{P}_m} \qquad 3.37$$

We will neglect the third term as it is a factor r_{lk}/λ smaller than the second one. We mention that the second term is the counterpart of the last quadratic term of 3.36.

The macroscopic moment densities $\underline{P}(\underline{R})$ and $\underline{Q}(\underline{R})$ can now be written as

$$\underline{P}(\underline{R}) = \overline{\underline{A}} \cdot \underline{E}^w(\underline{R}) + \overline{\underline{B}} : (\underline{\nabla E})^w(\underline{R}) \qquad 3.38$$

$$\underline{Q}(\underline{R}) = \overline{\underline{B}'} \cdot \underline{E}^w(\underline{R}) \qquad 3.39$$

$\overline{\underline{A}}$, $\overline{\underline{B}}$ and $\overline{\underline{B}'}$ are averaged polarizability densities corresponding to $\underline{\alpha}$, $\underline{\beta}$, and $\underline{\beta}'$.

$$\overline{\underline{A}} = \nu \left[\overline{\underline{\alpha}_k} - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l} - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} : \underline{\beta}'_l} - \sum_l{}' \overline{\underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \cdot \underline{\alpha}_l} \right. $$

$$+ \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lk} \cdot \underline{\alpha}_k} + \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{\nabla}_l \underline{T}_{kl} : \underline{\beta}'_l \cdot \underline{T}_{lk} \cdot \underline{\alpha}_k}$$

$$+ \sum_l{}' \overline{\underline{\beta}_k : \underline{\nabla}_k \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lk} \cdot \underline{\alpha}_k} + \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\beta}_l : \underline{\nabla}_l \underline{T}_{lk} \cdot \underline{\alpha}_k}$$

$$+ \left. \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{\nabla}_k \underline{T}_{lk} : \underline{\beta}'_k} \right] \qquad 3.40$$

$$\overline{\underline{B}} = \nu \left[\overline{\underline{\beta}_k} - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \underline{r}_{lk} \cdot \underline{\alpha}_l} - \sum_l{}' \overline{\underline{\alpha}_k \cdot (\underline{\nabla}_l \underline{T}_{kl}) \underline{r}_{lk} : \underline{\beta}'_l} \right.$$

$$- \sum_l{}' \overline{\underline{\beta}_k : (\underline{\nabla}_k \underline{T}_{kl}) \underline{r}_{lk} \cdot \underline{\alpha}_l} - \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\beta}_l}$$

$$+ \left. \sum_l{}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lk} \cdot \underline{\beta}_k} \right] \qquad 3.41$$

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$$\overline{\underline{B}'} = \nu \left[\overline{\underline{\beta}'_k} - \sum_l{'} \overline{\underline{\beta}'_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l} + \sum_l{'} \overline{\underline{\beta}'_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l \cdot \underline{T}_{lk} \cdot \underline{\alpha}_k} \right] \qquad 3.42$$

We have included all terms involving pair distribution functions up to the third order in the polarizabilities. Explicitly a term like $\nu \sum_l{'} \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \cdot \underline{\alpha}_l}$ reads as

$$\int \underline{\alpha}(\theta) \cdot \underline{T}(\underline{R}, \underline{R}') \underline{\alpha}(\theta') n_2(\underline{R}, \underline{R}', \theta, \theta') d\underline{R}' d\theta d\theta'.$$

CHAPTER 4

THE GENERAL WAVE EQUATION AND THE
EXTINCTION THEOREM

I n t r o d u c t i o n

In the equations:

$$\underline{P}(\underline{R}) = \underline{A} \cdot \underline{E}^w(\underline{R}) + \underline{B} : (\underline{\nabla}\underline{E})^w(\underline{R})$$

$$\underline{Q}(\underline{R}) = \underline{B}' \cdot \underline{E}^w(\underline{R})$$

$\underline{E}^w$ and $(\underline{\nabla}\underline{E})^w$ depend on the primary field and the polarizations everywhere in the medium. Thus they are relations between macroscopic quantities which have the form of integro-differential equations. It appears to be possible, however, to derive a differential equation for the moment densities $\underline{P}$ and $\underline{Q}$.

The usual procedure to effectuate this (e.g. Rosenfeld, 1951) consists in assuming for $\underline{P}$ a plane wave with constant amplitude and then to show that the internal field propagates in a similar way. An essential step in the derivation is the elimination of the primary field $\underline{E}^e$ which is annihilated by an integral over the outer surface of the medium (extinction theorem).

Hoek (1939), however, showed that for an isotropic medium without optical activity a more fundamental treatment is possible which consists in first deriving the wave equation and then proving the extinction theorem without specifying the wave motion.

For optically active media Hoek returns again to the first mentioned procedure, which is also followed by authors dealing with anisotropic media (Darwin, 1924; Mazur et al., 1955, 1956, 1959).

We will show that Hoek's method can be generalized for an anisotropic as well as optically active medium. Without speci-

fying the type of wave motion we will derive a differential
equation for the polarization density $\underline{P}$. With the aid of this
equation the extinction theorem, which is no longer necessary for
deriving the wave equation, follows.

A. **The differential equation for an
    arbitrary wave in an anisotropic
    optically active medium**

According to eq. 3.38 and 3.39:

$$\underline{P}(\underline{R}) = \underline{A} \cdot \underline{E}^w(\underline{R}) + \underline{B} : (\underline{\nabla}\underline{E})^w(\underline{R}) \qquad 4.1$$

$$\underline{Q}(\underline{R}) = \underline{B}' \cdot \underline{E}^w(\underline{R}) \qquad 4.2$$

where:

$$E_\alpha^w(\underline{R}) = E_\alpha^e(\underline{R}) + \int_{o(R)}^{V} \{(\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta}) Y(\underline{R},\underline{R}')\}\, P_\beta(\underline{R}')d\underline{R}'$$

$$+ \int_{o(R)}^{V} \{(\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta}) \nabla_\gamma' Y(\underline{R},\underline{R}')\}\, Q_{\beta\gamma}(\underline{R}')d\underline{R}' \qquad 4.3$$

$$(\nabla_\gamma E_\beta)^w(\underline{R}) = \nabla_\gamma E_\beta^e(\underline{R}) + \int_{o(R)}^{V} \{(\nabla_\beta \nabla_\delta + k^2 U_{\beta\delta}) \nabla_\gamma Y(\underline{R},\underline{R}')\} P_\delta(\underline{R}')d\underline{R}' \quad 4.4$$

∇_γ' means a differentiation at $\underline{R}'$, and ∇_γ at $\underline{R}$. V denotes the
outer boundary of the medium. $o(R)$ is a small sphere, centred at
$\underline{R}$, which is excluded from the integrations. After the integrations
the radius of this sphere is reduced to zero.

$$Y(\underline{R},\underline{R}') = \frac{1}{4\pi} \frac{e^{-ik|\underline{R}'-\underline{R}|}}{|\underline{R}'-\underline{R}|} \qquad 4.5$$

As products of third order polarizabilities are always ne-
glected we can combine 4.2 with 4.1:

$$\underline{Q}(\underline{R}) = \underline{B}' \cdot \underline{A}^{-1} \cdot \underline{P}(\underline{R}) \qquad 4.6$$

We need a number of formulae which are obtained through inte-
gration by parts:

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$$\int\limits_{o(R)}^{V} \{\nabla'_\gamma Y(\underline{R},\underline{R}')\}P_\delta(\underline{R}')d\underline{R}' = S^{(1)}_{\gamma\delta} - \int\limits_{o(R)}^{V} Y(\underline{R},\underline{R}')\nabla'_\gamma P_\delta(\underline{R}')d\underline{R}' \qquad 4.7$$

$$\int\limits_{o(R)}^{V} \{\nabla'_\beta \nabla'_\gamma Y(R,R')\}P_\delta(R')d\underline{R}' = S^{(2)}_{\beta\gamma\delta} + \frac{1}{3}\delta_{\beta\gamma}P_\delta(\underline{R})$$

$$+ \int\limits_{o(R)}^{V} Y(\underline{R},\underline{R}')\nabla'_\beta \nabla'_\gamma P_\delta(\underline{R}')d\underline{R}' \qquad 4.8$$

$$\int\limits_{o(R)}^{V} \{\nabla'_\alpha \nabla'_\beta \nabla'_\gamma Y(\underline{R},\underline{R}')\}P_\delta(\underline{R}')d\underline{R}' = S^{(3)}_{\alpha\beta\gamma\delta} - \frac{1}{5}(\delta_{\beta\gamma}\nabla_\alpha + \text{cycl.})P_\delta(\underline{R})$$

$$- \int\limits_{o(R)}^{V} Y(\underline{R},\underline{R}')\nabla'_\alpha \nabla'_\beta \nabla'_\gamma P_\delta(\underline{R}')d\underline{R}' \qquad 4.9$$

The surface integrals over the outer boundary Σ with normal unit vectors $\underline{u}$ are:

$$S^{(1)}_{\gamma\delta} = \int\limits^{\Sigma} Y(\underline{R},\underline{R}')u_\gamma P_\delta(\underline{R}')dS \qquad 4.10$$

$$S^{(2)}_{\beta\gamma\delta} = \int\limits^{\Sigma} \{\nabla'_\beta Y(\underline{R},\underline{R}')\}u_\gamma P_\delta(\underline{R}')dS - \int\limits^{\Sigma} Y(\underline{R},\underline{R}')u_\beta \nabla'_\gamma P_\delta(\underline{R}')dS \qquad 4.11$$

$$S^{(3)}_{\alpha\beta\gamma\delta} = \int\limits^{\Sigma} \{\nabla'_\alpha \nabla'_\beta Y(\underline{R},\underline{R}')\}u_\gamma P_\delta(\underline{R}')dS - \int\limits^{\Sigma} \{\nabla'_\alpha Y(\underline{R},\underline{R}')\}u_\beta \nabla'_\gamma P_\delta(\underline{R}')dS$$

$$+ \int\limits^{\Sigma} Y(\underline{R},\underline{R}')u_\alpha \nabla'_\beta \nabla'_\gamma P_\delta(\underline{R}')dS \qquad 4.12$$

With these equations 4.1 can be reduced to:

$$\mathcal{P}_1(\underline{R}) + \mathcal{C}(\underline{R}) + \mathcal{S}_1(\underline{R}) + \int\limits_{o(R)}^{V} Y(\underline{R},\underline{R}')\mathcal{P}_2(\underline{R}')d\underline{R}' = 0 \qquad 4.13$$

The following abbreviations are used:

$$\mathcal{P}_1(\underline{R}) = P_\alpha(\underline{R}) - \frac{1}{3}A_{\alpha\beta}P_\beta(\underline{R}) + \frac{1}{5}A_{\alpha\beta}B'_{\gamma\epsilon\delta}(A^{-1})_{\epsilon\mu}(\delta_{\beta\gamma}\nabla_\delta + \text{cycl.})P_\mu(\underline{R})$$

$$- \frac{1}{5}B_{\alpha\beta\delta}(\delta_{\beta\gamma}\nabla_\delta + \text{cycl.})P_\gamma(\underline{R}) \qquad 4.14$$

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$$\mathcal{E}(\underline{R}) = -A_{\alpha\beta}E^e_\beta(\underline{R}) - B_{\alpha\beta\gamma}\nabla_\gamma E^e_\beta(\underline{R}) \qquad 4.15$$

$$\mathcal{S}_1(\underline{R}) = -A_{\alpha\beta}S^{(2)}_{\beta\gamma\gamma} - A_{\alpha\beta}B'_{\gamma\epsilon\delta}(A^{-1})_{\epsilon\mu}\{S^{(3)}_{\beta\gamma\delta\mu} + k^2\delta_{\beta\gamma}S^{(1)}_{\delta\mu}\}$$

$$+ B_{\alpha\beta\delta}\{S^{(3)}_{\beta\gamma\delta\gamma} + k^2\delta_{\beta\gamma}S^{(1)}_{\delta\gamma}\} \qquad 4.16$$

$$\mathcal{P}_2(\underline{R}') = -A_{\alpha\beta}\{\nabla'_\beta\nabla'_\gamma + k^2U_{\beta\gamma}\}P_\gamma(\underline{R}')$$

$$+ A_{\alpha\beta}B'_{\gamma\epsilon\delta}(A^{-1})_{\epsilon\mu}\{\nabla'_\beta\nabla'_\gamma + k^2U_{\beta\gamma}\}\nabla'_\delta P_\mu(\underline{R}')$$

$$- B_{\alpha\beta\delta}\{\nabla'_\beta\nabla'_\gamma + k^2U_{\beta\gamma}\}\nabla'_\delta P_\gamma(\underline{R}') \qquad 4.17$$

Applying to eq. 4.13 the operator $(\triangle + k^2)$ leads to:

$$(\triangle + k^2)\mathcal{P}_1(\underline{R}) - \mathcal{P}_2(\underline{R}) = 0 \qquad 4.18$$

since this operator annihilates the primary field and its derivatives and also the integrals over the outer surface of the medium. At the same time use is made of:

$$(\triangle + k^2)\int_{o(R)}^{V} Y(\underline{R},\underline{R}')\,\mathcal{P}_2(\underline{R}')d\underline{R}' = -\mathcal{P}_2(\underline{R}) \qquad 4.19$$

(see Hoek, 1939, appendix).

Substituting the expressions for $\mathcal{P}_1$ and $\mathcal{P}_2$, the wave equation can be written as:

$$(\triangle + k^2)\left\{P_\alpha(\underline{R}) - \frac{1}{3}A_{\alpha\beta}P_\beta(\underline{R}) + \frac{1}{5}A_{\alpha\beta}B'_{\gamma\epsilon\delta}(A^{-1})_{\epsilon\mu}(\delta_{\beta\gamma}\nabla_\delta + \text{cycl.})P_\mu(\underline{R}) + \right.$$

$$\left. - \frac{1}{5}B_{\alpha\beta\delta}(\delta_{\beta\gamma}\nabla_\delta + \text{cycl.})P_\gamma(\underline{R})\right\} +$$

$$+ A_{\alpha\beta}\{\nabla_\beta\nabla_\gamma + k^2U_{\beta\gamma}\}P_\gamma(\underline{R}) +$$

$$- A_{\alpha\beta}B'_{\gamma\epsilon\delta}(A^{-1})_{\epsilon\mu}\{\nabla_\beta\nabla_\gamma + k^2U_{\beta\gamma}\}\nabla_\delta P_\mu(\underline{R}) +$$

$$+ B_{\alpha\beta\delta}\{\nabla_\beta\nabla_\gamma + k^2U_{\beta\gamma}\}\nabla_\delta P_\gamma(\underline{R}) = 0 \qquad 4.20$$

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For the general case of an anisotropic and optically active medium this is a rather intricate equation. In chapter 5 this equation will be applied to the case of an isotropic optically active medium.

B. Extinction theorem

The extinction theorem can be proved by substituting $(\Delta + k^2)\mathcal{P}_1(\underline{R}')$ for $\mathcal{P}_2(\underline{R}')$ under the integral sign of eq. 4.13. By application of Green's theorem, the integral can be reduced according to:

$$\int\limits_{o(R)}^{V} Y(\underline{R},\underline{R}')(\Delta + k^2)\mathcal{P}_1(\underline{R}') = \int\limits_{o(R)}^{V}\left[Y(\underline{R},\underline{R}')\Delta\,\mathcal{P}_1(\underline{R}') + \right.$$

$$\left. - \{\Delta Y(\underline{R},\underline{R}')\}\,\mathcal{P}_1(\underline{R}')\right]d\underline{R}'$$

$$= \int^{\Sigma}\left[Y(\underline{R},\underline{R}')\,\frac{\partial\mathcal{P}_1(\underline{R}')}{\partial\eta} - \left\{\frac{\partial Y(\underline{R},\underline{R}')}{\partial\eta}\right\}\mathcal{P}_1(\underline{R}')\right]dS$$

$$- \int^{s(R)}\left[Y(\underline{R},\underline{R}')\,\frac{\partial\mathcal{P}_1(\underline{R}')}{\partial\eta} - \left\{\frac{\partial Y(\underline{R},\underline{R}')}{\partial\eta}\right\}\mathcal{P}_1(\underline{R}')\right]dS \qquad 4.21$$

The surface integral over the small sphere is equal to $\mathcal{P}_1(\underline{R})$. The integral over the outer surface is abbreviated by $\mathcal{S}_2(\underline{R})$. $d\eta$ is a line element of the outward normal in a point of the surface in $\underline{R}'$-space ($\underline{R}$ is to be regarded as constant).

Substituting this result in eq. 4.13 leads to:

$$\mathcal{E}(\underline{R}) + \mathcal{S}_1(\underline{R}) + \mathcal{S}_2(\underline{R}) = 0 \qquad 4.22$$

which is the mathematical formulation of the extinction theorem.

CHAPTER 5

ISOTROPIC MEDIA

Introduction

In section A of this chapter the general theory is applied to an optically active isotropic medium. The limitations of our method are discussed in section B, where also the results for two simple models are given. In view of our results several recent papers on this subject are commented (section C).

A. Rotatory power of an isotropic medium

In case of isotropy the tensor $\underline{A}$ becomes the unit tensor multiplied by a scalar A_o; $\underline{B}$ and $\underline{B}'$ are reduced to the permutation tensor multiplied by constants B_o and B_o'.

$$\bar{A}_{\alpha\beta} = A_o U_{\alpha\beta} \qquad\qquad 5.1$$

$$\bar{B}_{\alpha\beta\gamma} = B_o [\alpha\beta\gamma] \qquad\qquad 5.2$$

$$\bar{B}'_{\alpha\beta\gamma} = B_o' [\alpha\beta\gamma] \qquad\qquad 5.3$$

If 5.3 is substituted in 4.2 it follows that:

$$Q_{\alpha\gamma} = - Q_{\gamma\alpha} \quad \text{and} \quad Q_{\alpha\alpha} = 0 \qquad\qquad 5.4$$

This means that in an isotropic medium the quadrupole moment, which depends on the symmetric part of $\underline{Q}$, vanishes (chapter 2D). Substitution of 5.1, 5.2 and 5.3 in 4.20 yields:

$$\left(1 - \frac{1}{3} A_o\right)(\Delta + k^2)P_\alpha + A_o\{\nabla_\alpha \nabla_\beta + k^2 U_{\alpha\beta}\} P_\beta$$

$$+ (B_o - B_o')k^2[\alpha\beta\gamma] \nabla_\gamma P_\beta = 0 \qquad 5.5$$

Multiplying 5.5 with ∇_α and summing over α gives:

$$\left(1 + \frac{2}{3} A_o\right)(\Delta + k^2)\nabla_\alpha P_\alpha = 0 \qquad 5.6$$

As $\underline{P}$ does not satisfy the same wave equation as $\underline{E}^e$ eq. 5.6 implies that:

$$\nabla_\alpha P_\alpha = 0 \qquad 5.7$$

if the assumption $A_o \neq -\frac{3}{2}$ holds.

Eq. 5.7 simplifies 5.5 to:

$$\Delta P_\alpha + k^2 \frac{1 + \frac{2}{3} A_o}{1 - \frac{1}{3} A_o} P_\alpha + k^2 \frac{B_o - B_o'}{1 - \frac{1}{3} A_o} [\alpha\beta\gamma] \nabla_\gamma P_\beta = 0 \qquad 5.8$$

We suppose now that there are solutions for $\underline{P}$ satisfying the wave equation:

$$(\Delta + n^2 k^2)\underline{P} = 0 \qquad 5.9$$

Substituted in 5.8 it follows that:

$$\left(n^2 - \frac{1 + \frac{2}{3} A_o}{1 - \frac{1}{3} A_o}\right)\underline{P} + \frac{B_o - B_o'}{1 - \frac{1}{3} A_o} \nabla \times \underline{P} = 0 \qquad 5.10$$

Applying the operator $\underline{\nabla} \times$ to this equation and using:

$$\underline{\nabla} \times \underline{\nabla} \times \underline{P} = \underline{\nabla}\underline{\nabla} \cdot \underline{P} - \Delta\underline{P} = -\Delta\underline{P} = n^2 k^2 \underline{P} \qquad 5.11$$

it follows:

$$\left(n^2 - \frac{1 + \frac{2}{3} A_o}{1 - \frac{1}{3} A_o}\right) \nabla \times \underline{P} + n^2 k^2 \frac{B_o - B_o'}{1 - \frac{1}{3} A_o} \underline{P} = 0 \qquad 5.12$$

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From the equations 5.10 and 5.12 it follows that:

$$\left(n^2 - \frac{1 + \frac{2}{3} A_o}{1 - \frac{1}{3} A_o}\right) = \pm \frac{B_o - B'_o}{1 - \frac{1}{3} A_o} nk \qquad 5.13$$

with the corresponding solutions:

$$\underline{P} \pm \frac{1}{nk} \nabla \times \underline{P} = 0 \qquad 5.14$$

The meaning of this result can perhaps best be illustrated by considering a plane wave travelling in the 3-direction:

$$\underline{P} = \underline{P}_o e^{-inkx_3} \qquad 5.15$$

In components 5.14 yields:

$$P_1 \pm iP_2 = 0 \qquad 5.16$$

With a right-handed choice of axes the + sign refers to a right-handed, the - sign to a left-handed circularly polarized wave. Calling the roots of 5.13 corresponding to the upper or lower sign n_+, n_-:

$$n_+ - n_- = \frac{B_o - B'_o}{1 - \frac{1}{3} A_o} k \qquad 5.17$$

The rotation of the plane of polarization follows from Fresnel's formula (cf. eq. 1.1):

$$\chi = \frac{\pi}{\lambda_{vac}} (n_- - n_+) \qquad 5.18$$

which becomes:

$$\chi = \frac{k^2}{2} \frac{B'_o - B_o}{1 - \frac{1}{3} A_o} \qquad 5.19$$

The right-hand side of 5.13 is very small with respect to the other terms in the equation. For example a rotation of 1 radian/cm

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implies that $(n_- - n_+)$ or $\dfrac{B_o' - B_o}{1 - 1/3\,A_o}\,k$ is of the order of magnitude of 10^{-5}, whereas n^2 is about 2. Therefore to a good approximation:

$$n^2 = \frac{1 + \frac{2}{3}A_o}{1 - \frac{1}{3}A_o} \quad \text{or} \quad \frac{1}{1 - \frac{1}{3}A_o} = \frac{n^2 + 2}{3} \qquad 5.20$$

Substitution in 5.19 yields:

$$\chi = \frac{k^2}{2}\left(\frac{n^2 + 2}{3}\right)(B_o' - B_o) \qquad 5.21$$

This equation has the same appearance as Hoek's final formula. It also contains the factor $\dfrac{n^2 + 2}{3}$ to the first power. The difference is that our constants B_o and B_o' incorporate the reaction field and correlation effects. Given our model eq. 5.21 is in principle exact, since B_o and B_o' can be calculated to any desired accuracy.

Although we have not explicitly dealt with mixtures it will be obvious how the present treatment can be extended to systems containing different molecules.

It may be of some interest to consider also other solutions of eq. 5.8 which more closely correspond to what happens in actual polarimetry. We introduce as a trial solution a plane wave, again travelling in the 3-direction but having a real amplitude which may also depend on x_3 ("linearly" polarized light with rotating plane of polarization):

$$\underline{P}(x_3) = \underline{P}_o(x_3)e^{-iknx_3} \qquad 5.22$$

Writing $\underline{u}$ for the unit vector in the 3-direction, the equation $\nabla \cdot \underline{P} = 0$, yields:

$$\underline{u} \cdot \underline{P}_o' - ikn\,\underline{u} \cdot \underline{P}_o = 0 \qquad 5.23$$

Since $\underline{P}_o$ and $\underline{P}_o'$ are real it follows that $\underline{u} \cdot \underline{P}_o = 0$, which implies that we have a transverse wave.

With the abbreviations:

$$\bar{n}^2 = \frac{1 + \frac{2}{3} A_o}{1 - \frac{1}{3} A_o} \quad \text{and} \quad \gamma = \frac{1}{2} \frac{B_o - B'_o}{1 - \frac{1}{3} A_o} k^2 \qquad 5.24$$

the wave equation becomes:

$$(\Delta + k^2 \bar{n}^2) \underline{P} - 2\gamma \underline{\nabla} \times \underline{P} = 0 \qquad 5.25$$

Substituting 5.22 in 5.25 yields:

$$\underline{P}''_o - 2ikn \, \underline{P}'_o + k^2(\bar{n}^2 - n^2)\underline{P}_o + 2ikn\gamma \underline{u} \times \underline{P}_o - 2\gamma \underline{u} \times \underline{P}'_o = 0 \quad 5.26$$

Writing the real and imaginary parts of this equation gives:

$$\underline{P}''_o + k^2(\bar{n}^2 - n^2)\underline{P}_o - 2\gamma \underline{u} \times \underline{P}'_o = 0 \qquad 5.27$$

$$\underline{P}'_o - \gamma \underline{u} \times \underline{P}_o = 0 \qquad 5.28$$

From these two equations $\underline{P}_o$ and the value of n can be derived. Scalar multiplication of 5.28 with $\underline{P}_o$ gives:

$$\underline{P}_o \cdot \underline{P}'_o = 0 \qquad 5.29$$

which implies that the absolute length of the vector $\underline{P}_o$ is constant. It is easily shown that the solution of 5.28 and 5.29 is:

$$(P_o)_1 = |P_o| \cos(\gamma x_3 + \psi) \qquad 5.30$$

$$(P_o)_2 = |P_o| \sin(\gamma x_3 + \psi) \qquad 5.31$$

This means that the angle χ (in radians/cm) over which the vector $\underline{P}_o$ ("plane of polarization") has rotated to the right is:

$$\chi = -\gamma \qquad 5.32$$

which is the same result as 5.19, as it should be of course.

Differentiation of eq. 5.28 together with this equation yields:

$$\underline{P}''_o + \gamma^2 \underline{P}_o = 0 \qquad 5.33$$

On the other hand the differentiated eq. 5.28 together with 5.27 gives:

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$$\underline{P}''_o + k^2(n^2 - \bar{n}^2)\underline{P}_o = 0 \qquad\qquad 5.34$$

These two equations imply that:

$$n^2 = \bar{n}^2 + \frac{1}{k^2}\gamma^2 \qquad\qquad 5.35$$

For all practical purposes $n = \bar{n}$.

B. Limitations and applications

It may be useful to recapitulate at this point the main characteristics of our model and to discuss its limitations. We consider the medium as an assembly of identical almost spherical molecules each of which is characterized by polarizability tensors $\underline{\alpha}$, $\underline{\beta}$ and $\underline{\beta}'$. An arbitrarily selected molecule has a position and orientation which is correlated with positions and orientations of other molecules within a sphere, the correlation sphere, about the selected molecule. With molecules outside this sphere no correlations have to be taken account of. This model of course is only of limited applicability.

A first limitation consists in the neglect of the dependence of polarizability terms on the density of the medium (Jansen-Mazur effect). The influence of this effect on the polarizability densities $\underline{B}$ and $\underline{B}'$ has not yet been studied. In a classical picture of the polarizability this effect is due to anharmonically bound electrons. Anharmonicity, however, is important in the one-electron model for optically active molecules (Condon et al., 1937). It consists of an anisotropic harmonic oscillator with an added cubic term in the potential energy.

Perhaps more serious is the deviation from the spherical shape. Here too, it is difficult to estimate the error introduced by our assumptions without explicit calculations. This point could be very important in the case of macromolecules, but on the other hand, phenomenologically the optical properties of systems with large molecules do not deviate essentially from systems with small molecules.

A drawback of our model is that in the final formula $\underline{B}$ and $\underline{B}'$ occur in the combination $B_o - B'_o$, which in our derivation of this formula is more or less fortuitous. In other derivations based on

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simpler models (Born, 1933; Kooy, 1936) or in some macroscopic derivations (Ramachandran, Ramaseshan, 1961) optical activity is described by one second order pseudo tensor (gyration tensor), which is not necessarily built up from two third order tensors.

Although the transition to an isotropic medium has not been made until chapter 5, the general formulae which have been given before, should not be applied to an anisotropic medium without caution. For the molecular distribution functions were supposed to depend on the distance between the molecules and not on the direction of the line connecting their centres.

Applications

As an illustration we will derive the expression for the optical activity of a molecule represented by coupled anisotropic polari- zabilities. This model has been studied extensively by Born (1933), Kuhn (1932), Kooy (1936) and Kirkwood (1937). To this model we can apply equation 3.41 neglecting all β and β'-tensors and considering a molecule as an assembly of almost spherical units with anisotropic polarizabilities $\underline{\alpha}$, interacting through dipole-dipole forces. The fact that the units constitute an opti- cally active molecule shows up in a strong correlation between positions and orientations of the units. In this description the molecule may be rigid as well as flexible. Neglecting correlations between molecules, eq. 3.41 applied to the present model yields:

$$B_o = - \nu \sum_{k, l=1}^{j} {}' \overline{\underline{\alpha}_k \cdot \underline{T}_{kl} \underline{r}_{lk} \cdot \underline{\alpha}_l} \qquad 5.36$$

where j is the number of units in a molecule and ν is the number of molecules in 1 cc. This equation can be simplified by assuming that the polarizabilities are linear along the unit vectors $\underline{b}_k$ and $\underline{b}_l$:

$$\underline{\alpha}_k = \sigma_k \underline{b}_k \underline{b}_k \qquad 5.37$$

$$\underline{\alpha}_l = \sigma_l \underline{b}_l \underline{b}_l \qquad 5.38$$

Introducing (cf. Looyenga, 1955):

$$S_{kl} = \frac{1}{4\pi r_{lk}^5} \{3(\underline{b}_k \cdot \underline{r}_{lk})(\underline{b}_l \cdot \underline{r}_{lk}) - r_{lk}^2(\underline{b}_l \cdot \underline{b}_k)\} \qquad 5.39$$

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$$D_{kl} = \overline{\underline{b}_k \underline{b}_l r_{lk}} = \frac{1}{6} [\underline{b}_k \times \underline{b}_l] \cdot \underline{r}_{lk}$$ 5.40

we find:

$$B_o = -\nu \sum_{k,\,l=1}^{j}{}' \sigma_k \sigma_l S_{kl} D_{kl}$$ 5.41

In molecules where all groups attached to an asymmetric carbon atom have axial symmetry about the bond joining them to the asymmetric centre, these pairwise interactions contribute nothing to the optical activity (Kauzmann and Eyring, 1941; Kauzmann, Clough and Tobias, 1961). In that case higher approximations of eq. 3.41 should be used.

As a second illustration we will for a simple case derive an approximation to the reaction field. Let us omit the correlation between the particles except that they can be approximated as hard spheres which can not approach more closely than a molecular diameter. In addition we will assume that the $\underline{\alpha}$ polarizabilities are isotropic. From eq. 3.41 it follows:

$$\overline{B}_{\alpha\beta\gamma} = \nu\beta_o [\alpha\beta\gamma] - \nu\sum_l{}' \alpha_o^2 \overline{T_{\alpha\beta}^{(kl)} r_\gamma^{(lk)}}$$

$$- \nu\sum_l{}' \alpha_o \overline{\nabla_\epsilon^{(l)} T_{\alpha\delta}^{(kl)} r_\gamma^{(lk)}}[\delta\beta\epsilon]\beta_o'$$

$$- \nu\sum_l{}' \beta_o [\alpha\delta\epsilon] \overline{\nabla_\epsilon^{(k)} T_{\delta\beta}^{(kl)} r_\gamma^{(lk)}} \alpha_o - \nu\sum_l{}' \alpha_o \overline{T_{\alpha\delta}^{(kl)}}[\delta\beta\gamma]\beta_o$$

$$+ \nu\sum_l{}' \alpha_o^2 \overline{T_{\alpha\delta}^{(kl)} T_{\delta\epsilon}^{(lk)}}[\epsilon\beta\gamma]\beta_o$$ 5.42

The second and fifth term can easily be shown to vanish (see appendix). The third is zero because the averaged fourth order tensor is symmetric in the indices δ and ϵ, while the permutation tensor is antisymmetric in these indices. For similar reasons the fourth term is zero. The sixth term, which represents the first approximation to the reaction field does not vanish:

$$\overline{T_{\alpha\delta}^{(kl)} T_{\delta\epsilon}^{(lk)}} = \frac{1}{48\pi V} \frac{1}{a^3} \delta_{\alpha\epsilon}$$ 5.43

where V is the volume of the medium and a is the radius of a

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molecule (see Kirkwood, 1936; Kirkwood's $\underline{T}$ is 4π times the tensor $\underline{T}$ used by us). Summing 5.43 over all particles and substituting in 5.42 yields:

$$\bar{B}_{\alpha\beta\gamma} = \nu\beta_o \left\{ 1 + \frac{a_o^2\nu}{48\pi a^3} \right\} [\alpha\beta\gamma] \qquad 5.44$$

Similarly 3.42 yields:

$$\bar{B}'_{\alpha\beta\gamma} = \nu\beta'_o \left\{ 1 + \frac{a_o^2\nu}{48\pi a^3} \right\} [\alpha\beta\gamma] \qquad 5.45$$

Aslanian and Vol'kenshtein (1959) also calculate the reaction field in order to study theoretically the influence of solvent on optical activity. They use a more specialized model than we do. This results in a correction term which has the same shape but is less simple than ours.

C. C o m m e n t   o n   r e c e n t   p u b l i c a t i o n s

I. Goossens (1958)
In his thesis Goossens aims at improving Hoek's theory on optical activity by reformulating the theory in such a way that Onsager-Böttcher's concept of the internal field can be used. Hoek shows why the part $(\nabla E)^w$ equal to $(\nabla \times \underline{E})^w$ differs from $\nabla \times \underline{E}^w$, but is equal to $\nabla \times \underline{E}$, where $\underline{E}$ is the average field which occurs in Maxwell's equations. His proof is given for the model leading to Lorentz' local field. Goossens remarks that, in our notation, $(\nabla \times \underline{E})^w$ is equal to $-\frac{1}{c}\dot{\underline{B}}^w$, where $\underline{B}^w$ is the working magnetic induction. Since the diamagnetism of a liquid implies only a very slight difference between $\underline{B}^w$ and $\underline{B}$, this entails that $(\nabla \times \underline{E})^w$ is $(\nabla \times \underline{E})$. As this is a very general result it also holds for the Onsager-Böttcher model.

Goossens' fundamental equation (Goossens ID11 or ID16) can be written as:

$$(n^2 - 1)\underline{E}(\underline{R}, t) = 4\pi\nu\sigma G(n)\underline{E}(\underline{R}, t) + 8\pi\nu\sigma' ikn[\underline{u} \times \underline{E}(\underline{R}, t)] \qquad 5.46$$

For comparison we reproduce our eq. 5.10:

$$(n^2 - 1)\underline{P}(\underline{R}) = A_o \frac{n^2 + 2}{3} \underline{P}(\underline{R}) + (B_o - B'_o)ikn[\underline{u} \times \underline{P}(\underline{R})] \qquad 5.47$$

$4\pi\sigma$ in eq. 5.46 corresponds to α_o of our theory and $8\pi\sigma'$ to $(\beta_o - \beta'_o)$. $G(n)$ is a factor dependent on the refractive index which converts the average field into the internal field. In the Lorentz approximation $G(n) = \frac{n^2 + 2}{3}$, whereas $A_o = \nu\alpha_o$ and $B_o - B'_o = \nu(\beta_o - \beta'_o)$. In this case both formulae are the same. If the Onsager-Böttcher model is applied:

$$G(n) = \frac{3n^2}{2n^2 + 1} \cdot \frac{1}{1 - f\sigma} \qquad 5.48$$

where:

$$f = \frac{1}{a^3} \frac{2n^2 - 2}{2n^2 + 1} \qquad 5.49$$

and a is the radius of the cavity in which a molecule is embedded. $G(n)$ involves the influence of the reaction field. According to Goossens only the internal field [*] as far as it works on σ is affected. This has a definite influence on the final formula for the optical activity. Numerically it becomes practically independent of the refractive index.

According to our eq. 5.21, however, reaction field and correlation effects only show up through their influence on $(B_o - B'_o)$ whereas the dependence on rotation of refractive index remains unchanged. Although the origin of this discrepancy is difficult to analyse, it may be that those terms in B_o which have $\underline{\alpha}_k$ as the first factor are contained implicitly in Goossens' factor $G(n)$. It may be also that the neglect of the difference between $\underline{B}^w$ and $\underline{B}$ is not sufficiently warranted.

II. Aslanian and Vol'kenshtein (1959)

These authors study the influence of solvent on optical activity. They consider the interactions between an optically active molecule consisting of two coupled anisotropic polarizabilities

[*] It should be noted that internal field here means the field actually polarizing the molecule. It differs from our definition of the internal field (see p. 29).

with a solvent molecule having an isotropic polarizability. Three corrections to the Lorentz approximation are introduced.

As a first correction they calculate the indirect coupling of the anisotropic polarizabilities via solvent molecules. The result is an intricate equation which has the same general appearance as our reaction field correction (eq. 5.44 and 5.45).

As a second correction changes in the anisotropic group polarizabilities due to inductive effects of the environment are introduced. However, if the resulting equation (eq. 16) is averaged, no change in the polarizabilities remains.

As a third correction Aslanian and Vol'kenshtein introduce hyperpolarizabilities of the different groups. This means that the polarizabilities depend on the static field of the dipole moments of other molecules. As we did not introduce the change of the polarizability in our theory, we will not discuss this point further.

III. *Venkataraman (1961)*

The starting point of this author is the polarizability theory as applied by Ramachandran to the rotatory power of β-quartz and some other crystals. Small molecules as well as polymers are assumed to consist of groups with second order polarizabilities only. For this model Venkataraman arrives at an equation which is similar to our eq. 5.41 which was obtained by specializing our general equation (chapter 5B) for the same model.

APPENDIX

In chapter 3 (p. 32) it has been stated without proof that in a number of integrals a spherical region does not contribute to the value of these integrals. The integrals are:

$$\underline{I}_1 = \nu^{-2} \int\limits^{V} \underline{F}(\underline{R},\underline{R}')n_2(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}')d\underline{R}' \qquad \text{A1}$$

$$\underline{I}_2 = \nu^{-2} \int\limits^{V} \underline{H}(\underline{R},\underline{R}')n_2(\underline{R},\underline{R}') : \underline{Q}(\underline{R}')d\underline{R}' \qquad \text{A2}$$

$$\underline{I}_3 = \nu^{-2} \int\limits^{V} \nabla_R \underline{F}(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}')d\underline{R}' \qquad \text{A3}$$

The radius of the sphere which has its centre at $\underline{R}$ should be small with respect to the wave length of light. Small means that if the integral over the spherical region is expanded in powers of k, terms with powers > 1 can be neglected.

In order to simplify the proof we assume that $\underline{P}$ and Q can be represented by plane waves:

$$\underline{P}(\underline{R}') = \underline{P}(\underline{R})\exp\{ik\underline{n}(\underline{R}-\underline{R}')\} \qquad \text{A4}$$

$$Q(\underline{R}') = Q(\underline{R})\exp\{ik\underline{n}(\underline{R}-\underline{R}')\} \qquad \text{A5}$$

where $\underline{n}$ is n times the unit vector in the direction of the wave. n is the refractive index.

Expanding $\underline{F}(\underline{R},\underline{R}') \cdot \underline{P}(\underline{R}')$ to the first power in k, yields:

$$F_{\alpha\beta}(o,r)P_{\beta}(r) = \frac{1}{4\pi} \left[\frac{1}{r^3} (3b_\alpha b_\beta - \delta_{\alpha\beta}) + \right.$$

$$\left. - ik \frac{n_\gamma}{r^2} (3b_\alpha b_\beta b_\gamma - \delta_{\alpha\beta}b_\gamma) \right] P_\beta(o) \qquad \text{A6}$$

where $\underline{b}$ is a unit vector pointing from $\underline{R}$ to $\underline{R}'$ and $r = |\underline{R}'-\underline{R}|$. If now we integrate over the polar angles θ and φ, the term independent of k and the term proportional to k vanish. The higher order terms may be neglected according to our assumption.

Similarly for $\underline{I}_2$ we develop $\underline{H}(\underline{R},\underline{R}') : \underline{Q}(\underline{R}')$ which becomes:

$$H_{\alpha\beta\gamma}(o,r)Q_{\beta\gamma}(r) = \frac{1}{4\pi}\left[\frac{1}{r^4}\{-15b_\alpha b_\beta b_\gamma + 3(b_\gamma\delta_{\alpha\beta} + b_\beta\delta_{\alpha\gamma} + b_\alpha\delta_{\beta\gamma})\}\right.$$

$$+ \frac{ikn_\delta}{r^3}\{15b_\alpha b_\beta b_\gamma b_\delta - 3(b_\delta b_\gamma\delta_{\alpha\beta} + b_\delta b_\beta\delta_{\alpha\gamma} + b_\delta b_\alpha\delta_{\beta\gamma})\}\left.\right]Q_{\beta\gamma}(o) \quad \text{A7}$$

Again terms independent of k and proportional to k disappear after integration over a spherical shell. This result applies immediately to $\underline{I}_3$ as:

$$\nabla_R \underline{F}(\underline{R},\underline{R}') = -\underline{H}(\underline{R},\underline{R}') \quad\quad\quad \text{A8}$$

In addition we have to prove that:

$$\overline{T_{kl}} = 0 \quad\quad\quad \text{A9}$$

$$\overline{T_{kl}\tau_{lk}} = 0 \quad\quad\quad \text{A10}$$

$$\overline{\nabla_l T_{kl}} = 0 \quad\quad\quad \text{A11}$$

$$\overline{\nabla_l T_{kl}\tau_{lk}} = 0 \quad\quad\quad \text{A12}$$

These equations hold since in each case integration of the expression under the bar over polar angles gives zero. This can be shown by straightforward calculations or more elegantly by symmetry considerations.

NOTATION AND SYMBOLS

The description of the optical rotatory power requires scalar quantities and cartesian tensors of the first, second and third rank. In some equations the tensors are written in components. As much as possible the first five characters of the Greek alphabet are used as suffixes. The summation convention is applied which means that one has to sum over the three values of an index if it appears twice (contraction).

We also use a shorthand notation where all vector and tensor quantities are underlined. The dyadic product of two tensors of arbitrary rank is denoted by writing one next to the other without a connecting sign in between. A dot between two tensors indicates a contraction, a colon a double contraction. For example $\underline{\nabla} \underline{E}^e$ in eq. 3.7 is a second order tensor and $\underline{\nabla} \cdot \underline{E}^e = \text{div} \underline{E}^e$ is a scalar. This notation, however, is not unambiguous as it does not show which indices are contracted. To avoid confusion some of the equations are given in both notations.

List of symbols

$\underline{A}$	second order polarizability tensor density	$\underline{B}, \underline{B}^w$	macroscopic, internal magnetic induction
$A_{\alpha\beta}^{kl}$	interaction tensor between particles k and l	C	normalisation constant
		D_{kl}	auxiliary function
A_o	scalar polarizability density	$\underline{D}$	dielectric displacement
$\underline{B}, \underline{B}'$	third order polarizability tensor densities	$\underline{E}, \underline{E}^e$	macroscopic, external electric field strength
B_o, B_o'	scalar polarizability densities	$(\underline{E})^w$	internal electric field
		$(\underline{\nabla}\underline{E})^w$	internal derivative of the electric field

$\underline{E}^d$	auxiliary electric field
E_m, E_n	energy levels
$\underline{F}$	dynamic dipole-dipole interaction tensor
$G(n)$	auxiliary function of n
$\underline{H}$	dynamic interaction tensor
$\underline{H}$	macroscopic magnetic field strength
$\underline{I}$	auxiliary integrals
M	molecular weight
$\underline{M}$	macroscopic magnetic dipole density
N	total number of molecules in the system
$\underline{P}$	macroscopic electric dipole density
$\underline{P}_{nm}$	electric dipole transition moment

Q	macroscopic higher moment density
$\underline{R}, \underline{R}', \underline{R}_k$	position vectors
R_{12}	$|\underline{R}' - \underline{R}|$
R_A	distance of A to molecular centre
S_{kl}	auxiliary function
$S(\ )$	surface integrals over the outer boundary
dS	surface element
$\underline{T}_{kl}$	static dipole-dipole tensor
T	absolute temperature
$\underline{U}$	second order unit tensor
U_o	intermolecular energy
V	volume of the medium
$\underline{W}, \underline{W}'$	auxiliary vectors
$Y(R_{12})$	Green's function

a	radius of a sphere
$\underline{a}$	vector potential
$\underline{b}$	unit vector
c	velocity of light in vacuo
d_o	density
e_i	charge of particle i
$\underline{e}$	microscopic electric field strength
f	distribution function
f	function of n
$g(R_{12})$	distribution function
$h(R_{12})$	distribution function
$2\pi\hbar$	Planck's constant
$\underline{h}$	microscopic magnetic field strength
i	$\sqrt{-1}$
$\underline{i}$	current density

k	$\dfrac{2\pi}{\lambda} = \dfrac{\omega}{c}$
$\underline{k}$	quadrupole moment
m_i	mass of particle i
$\underline{m}$	magnetic dipole moment
i, j, k, l, m	particle indices
$n, \bar{n}$	refractive indices
$\underline{n}$	n times unit vector in direction of the wave
$n_{..}(\underline{R}, ..)$	distribution functions
m, n	numbering of wave functions
$o(R)$	volume of a small sphere at $\underline{R}$
$\underline{P}'_B$	dipole moment density at B

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$\underline{p}_k$	dipole moment of particle k	$\underline{r}_B$	position vector of B in the molecular space
$(\underline{p}_i)_{op}$	momentum operator of particle i	$s(R)$	surface of a small sphere at $\underline{R}$
$\underline{q}_k$	higher moment of particle k	t	time
r_{AB}	distance between A and B	$\underline{u}$	unit vector
$\underline{r}_{lk}$	distance vector pointing from k to l	$\underline{v}$	charge velocity
		$\underline{x}, \underline{x}'$	position vectors in the molecular space
		$\underline{z}$	Hertz potential
$\alpha, \beta, \gamma,$		λ	wave length
δ, ϵ, μ	coordinate indices	ν	number density
α_o	scalar polarizability	ρ	charge density
$\underline{\alpha}$	second order polarizability tensor	Σ	macroscopic surface
		σ_k	scalar polarizability constant
$[\alpha\beta\gamma]$	permutation tensor		
$\underline{\beta}, \underline{\beta}'$	third order polarizabilities	$\underline{\sigma}(\underline{x}, \underline{x}')$	polarizability tensor density
β_o, β_o'	scalar polarizabilities	ϕ_n, ϕ_m	wave functions
γ	angle	Φ	scalar potential
$\delta(\underline{R}_i - \underline{R})$	Dirac δ-function	χ	rotation angle
$\delta_{\alpha\beta}$	Weierstrass symbol	ψ	phase angle
ζ, ζ_{nn}	auxiliary functions	ω	circular frequency
$d\eta$	line element of a normal vector	∇	Nabla operator
		Δ	Laplace operator
$\underline{\eta}(\underline{x}, \underline{x}')$	polarizability tensor density	$*$	complex conjugate
θ	orientation parameters of a molecule	$\mathcal{P}$	function of $\underline{P}$
		$\mathcal{E}$	function of $\underline{E}^e$
κ	Boltzmann's factor	$\mathcal{S}$	function of surface integrals

REFERENCES CITED IN PART ONE

Aslanian, V.M., Vol'kenshtein, M.V., Opt. Spectry (English Transl.) 7 132, 1959

Born, M., Optik, Julius Springer Verlag, Berlin, 1933

Born, M., Ann. Physik 55 177-240, 1918

Böttcher, C.J.F., Theory of Electric Polarisation, Elsevier Publ. Comp., Amsterdam, 1952

Brown, W.F., Handbuch der Physik XVII, Springer Verlag, Berlin, 1956

Condon, E.U., Altar, W., Eyring, H., J. Chem. Phys. 5 753, 1937

Darwin, C.G., Trans. Cambr. Phil. Soc. 23 137, 1924

Ewald, P.P., Thesis München, 1912

Ewald, P.P., Ann. Physik 49 1, 117, 1916

Eyring, H., Walter, J., Kimball, G.E., Quantum Chemistry, Wiley, New York, 1949

Goossens, W.J.A., Thesis Leiden, 1958

Jansen, L., Mazur, P., Physica 21 193, 1955

Jeffreys, H., Jeffreys, B.S., Methods of Mathematical Physics, Cambridge Univ. Press, Cambridge, 1956

Heitler, W., Quantum Theory of Radiation, Clarendon Press, Oxford, 1954

Hoek, H., Thesis Leiden, 1939

Hoek, H., Physica 8 209, 1941

Kauzmann, W., Clough, F.B., Tobias, I., Tetrahedron 13 57, 1961

Kauzmann, W., Eyring, H., J. Chem. Phys. 9 41, 1941

Kirkwood, J.G., J. Chem. Phys. 4 592, 1936

Kirkwood, J.G., J. Chem. Phys. 5 479, 1937

Kooy, J.M.J., Thesis Leiden, 1936

Kramers, H.A., Quantentheorie des Elektrons und der Strahlung, Akad. Verlag, Leipzig, 1938 (German edition). Quantum Mechanics, North-Holland Publ. Comp. Amsterdam, 1957 (English edition)

Kuhn, W., Freudenberg, K., Hand- und Jahrbuch der chemischen Physik 8 III, Leipzig 1936 (published before in 1932)

Lorentz, H.A., Wiedem. Ann. 9 641, 1880

Lorentz, H.A., Proc. Acad. Sci., Amsterdam, 254, 1902; Enc. Math. Wiss. Vol II, No 1, 200

Lorentz, H. A., Theory of Electrons, Dover publ., New York, 1952 (originally 1915)

Lorenz, L., Wiedem. Ann. 11 70, 1881

Looyenga, H., Thesis Leiden, 1955

Malleman, R. de, Ann. Phys. (Paris) 2 137, 1924

Malleman, R. de, Ann. Phys. (Paris) 4 456, 1925

Mazur, P., Jansen, L., Physica 21 208, 1955

Mazur, P., Mandel, M., Physica 22 289, 1956

Mazur, P., Mandel, M., Physica 22 299, 1956

Mazur, P., Postma, B. J., Physica 25 251, 1959

Oseen, C. W., Ann. Physik 48 1, 1915

Phillips, M., Handbuch der Physik IV, Springer Verlag, Berlin, 1962

Postma, B. J., Thesis Amsterdam, 1959

Ramachandran, G. N., Ramaseshan, S., Crystal Optics, Handbuch der Physik XXV/1 Section 36, Springer Verlag, Berlin, 1961

Rose, M. E., Elementary Theory of Angular Momentum, Wiley, New York, 1957

Rosenfeld, L., Z. Physik 52 161, 1928

Rosenfeld, L., Theory of Electrons, North-Holland Publ. Comp., Amsterdam, 1951

Stratton, J. A., Electromagnetic Theory, McGraw-Hill, New York, 1941

Venkataraman, S., Z. Naturforsch. 16a 356, 1961

Vol'kenshtein, M. V., Zh. Eksperim. i. Teor. Fiz. 20 342, 1950

Yvon, J., Act. Scient. Ind. n° 542, Fluctuations en Densité, Hermann et Cie, Paris, 1937 (I)

Yvon, J., Act. Scient. Ind. n° 543, La Propagation et la Diffusion de la Lumière, Hermann et Cie, Paris, 1937 (II)

PART TWO

KERR EFFECT APPLIED TO CONFORMATIONAL ANALYSIS

CHAPTER 6

INTRODUCTION

When a homogeneous isotropic transparant medium is placed in a strong electric field, it becomes birefringent. This phenomenon is known as the electro-optical Kerr effect (Kerr, 1875). Let us consider a beam of light which passes through the medium in a direction perpendicular to the static electric field. The components of the light with the electric vector parallel to the static electric field and the one vibrating perpendicular to the field, propagate with different velocities resulting in a phase difference Δ. This phase difference is proportional to the light path l and to the square of the electric field E. The proportionality constant B, which is called the Kerr constant is defined by:

$$\Delta = 2\pi B l E^2 \qquad 6.1$$

Usually Δ is given in radians, l in cm. and E in e.s.u.. B depends on the nature of the medium, its temperature and density and moreover on the wave length of the light.*)

Δ is also proportional to the difference in refractive index $(n_p - n_s)$ of light vibrating parallel and perpendicular to the electric field:

$$\Delta = \frac{2\pi l (n_p - n_s)}{\lambda} \qquad 6.2$$

where λ is the wave length of the light in vacuo. Combining 6.1 and 6.2 yields:

$$B = \frac{(n_p - n_s)}{\lambda} \frac{1}{E^2} \qquad 6.3$$

To indicate orders of magnitude B can amount from 7.10^{-9} for

*) In part two of this thesis we use electrostatic units.

liquid carbon tetrachloride to 4.10^{-5} for liquid nitrobenzene (both at room temperature for yellow light). Moreover it may be positive as well as negative.

The results of measurements on gases are usually expressed with another Kerr constant:

$$K = \frac{B\lambda}{n} = \frac{n_p - n_s}{n} \frac{1}{E^2} \qquad 6.4$$

where n is the refractive index of the medium. K has the advantage of being practically independent of the wave length.

For liquids the molecular Kerr constant is used:

$$_mK = \frac{6\lambda n B M}{(n^2 + 2)^2(\epsilon + 2)^2 d} \qquad 6.5$$

where M is the molecular weight, ϵ is the dielectric constant and d is the density of the medium. Sometimes the factor 6 is omitted. It is supposed that to a first approximation this constant $_mK$ characterizes the molecule independent of its state of aggregation.

The counter part of the Kerr effect is the electric dichroism. Both effects give in principle the same information since from a complete knowledge of the dispersion of the Kerr effect the electric dichroism can be calculated by the Kramers-Kronig relations and vice versa. Unlike the similar situation in optical rotation where the dispersion of optical activity can be measured through an absorption band, the determination of electric birefringence is practically unfeasible in a region where absorption occurs. Although the study of electric dichroism has become possible since the pioneering work of Kuhn et al. (1939), Liptay and Czekalla (1960) and Labhart (1961), and its theoretical interpretation has certain advantages, its application is restricted to those substances that have easily accessible absorption bands.

In gases and liquids the electric birefringence is mainly due to an orientation of optically anisotropic molecules. If the molecules have a permanent dipole moment its coupling with the static field will in the first place determine the degree of

orientation. Usually smaller in magnitude is the coupling of the anisotropic static polarizability with the electric field.

In the solid state orientation of molecules may still occur but generally the electric birefringence will be due to a deformation of the molecules and of the crystal lattice. Deformation effects may also play a role in the Kerr effect of isotropic molecules like CH_4, CCl_4 and A in the gaseous state. It may also be that other more subtle explanations apply in these cases. In the liquid state the molecular distributions may become anisotropic (anisotropic electrostriction).

Our measurements pertain to dipole molecules only, so that our considerations will be restricted to orientation effects. Without going into details one can say that the Kerr effect gives information about the molecular shape. In a flexible molecule it may contribute to the conformational analysis. For this purpose the measurement of the Kerr effect is not sufficient since the interpretation requires also the knowledge of dipole moment, average polarizability and depolarization factor. These additional data can be obtained in favourable cases from measurements of dielectric constant, refractive index and light scattering. In other cases some of the data have to be estimated, for instance with the aid of additivity rules.

A detailed theoretical interpretation is well-founded for measurements on gases, but here the experiments are difficult and the results lack sufficient accuracy. Moreover many chemical compounds have too low a vapour pressure at normal temperature and decompose at higher temperatures. With liquids the measurements are less difficult but the theoretical interpretation is hampered by the insufficient knowledge about the electric field working on an individual molecule. This difficulty appears twice. First in estimating the field that actually orients a molecule. Secondly the polarizing field of a light wave is not exactly known.

As a solution to these problems we have assumed that the formulae which apply for the gas phase can also be used for considerations of the liquid phase if the local fields are calculated according to the Lorentz model. Some authors (Klages, 1952; Steppuhn, 1956; Narayana Rao, 1958) use a model of the Onsager-Böttcher type. Because of the uncertainties of some of the assumptions (e.g. shape of the cavity, effective "dielectric constant" of the molecular substance) we did not consider it worth-while to introduce refinements which go beyond the Lorentz model.

For a gas of not too high density the refractive index of a light wave is related to the polarizability of the molecules by the Lorentz-Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha \qquad\qquad 6.6$$

N is the number of molecules per cc., α is the mean polarizability.

In the case of electric double refraction this equation has to be replaced by two equations, one for light vibrating parallel (6.7), the other for light vibrating perpendicularly (6.8) to the static electric field.

$$\frac{n_p^2 - 1}{n_p^2 + 2} = \frac{4\pi}{3} N\alpha_p \qquad\qquad 6.7$$

$$\frac{n_s^2 - 1}{n_s^2 + 2} = \frac{4\pi}{3} N\alpha_s \qquad\qquad 6.8$$

α_p and α_s are the mean polarizabilities in parallel and perpendicular directions. The problem is now to relate these polarizabilities to the anisotropic polarizabilities of the individual molecules.

Each molecule is characterized by a dipole moment, a static and an optical polarizability tensor (visualized as polarizability ellipsoids). Usually it is assumed that the principal axes of polarizability are the same for static as well as for optical polarizabilities. Moreover a relation suggested by Gans (1921) is used stating that the optical polarizability is equal to the static polarizability times a factor which depends on the frequency of the light. The static polarizabilities along the principal axes are denoted by $\bar{\alpha}_1, \bar{\alpha}_2, \bar{\alpha}_3$, the optical polarizabilities by $\alpha_1, \alpha_2, \alpha_3$. The components of the dipole moment along the same axes are μ_1, μ_2, μ_3.

The mean polarizabilities α_p, α_s are obtained by averaging the molecular polarizabilities over all orientations each with its proper Boltzmann factor. The procedure is somewhat more complicated but essentially similar to that followed in the theory of

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dielectric polarization. If the expressions for the mean polari-
zabilities are substituted in the equations 6.7 and 6.8, the
difference of these equations gives the Kerr constant[*]:

$$K = \frac{\pi}{27} \left(\frac{n^2 + 2}{n} \right)^2 (\epsilon + 2)^2 N(\theta_1 + \theta_2)$$ 6.9

with

$$\theta_1 = \frac{1}{45kT} \left[(\bar{a}_1 - \bar{a}_2)(\alpha_1 - \alpha_2) + (\bar{a}_2 - \bar{a}_3)(\alpha_2 - \alpha_3) + \right.$$
$$\left. + (\bar{a}_3 - \bar{a}_1)(\alpha_3 - \alpha_1) \right]$$ 6.10

$$\theta_2 = \frac{1}{45k^2T^2} \left[(\mu_1^2 - \mu_2^2)(\alpha_1 - \alpha_2) + (\mu_2^2 - \mu_3^2)(\alpha_2 - \alpha_3) + \right.$$
$$\left. + (\mu_3^2 - \mu_1^2)(\alpha_3 - \alpha_1) \right]$$ 6.11

ϵ is the dielectric constant. θ_1 is called the anisotropy term,
θ_2 is the dipole term.

In principle it is possible to determine θ_1 and θ_2 separately
from the temperature dependence of the Kerr constant. As θ_2 is
often much larger than θ_1, this method is inaccurate. Therefore a
different procedure is accepted. With the Gans relation:

$$\frac{\bar{a}_1}{a_1} = \frac{\bar{a}_2}{a_2} = \frac{\bar{a}_3}{a_3} = \frac{\bar{a}}{a} = \frac{n_\infty^2 - 1}{n^2 - 1} \simeq \frac{n_\infty - 1}{n - 1}$$ 6.12

θ_1 becomes:

$$\theta_1 = \frac{1}{45kT} \frac{n_\infty - 1}{n - 1} \left[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2 \right]$$ 6.13

The expression between brackets can be derived from the degree of
depolarization of Rayleigh scattering. n_∞ is the refractive
index for infinite wave length which includes the influence of
infrared absorptions.

From the knowledge of θ_1 and θ_2, which can now be calculated
from the Kerr constant K, one can determine α_1, α_2 and α_3 sepa-
rately if the mean polarizability, the dipole moment and its
orientation with respect to the principal axes are also known.

[*] Debye and Sack (1934) give the derivation which was originally
formulated by Langevin (1910) and Born (1918).

If the Gans relation holds or nearly holds θ_1 is always positive. A negative sign for K can only be caused by the dipole term θ_2. For example in chloroform where the dipole lies along the axis of the least polarizability, the Kerr constant is negative. As θ_1 and θ_2 have a different temperature dependence, it may happen that the Kerr constant changes sign at a certain temperature (e.g. ethylalcohol).

Molecular Kerr constants from measurements on solutions

For dilute solutions Briegleb (1931) suggested the following formula:

$$_mK_{12} = {_mK_1}f_1 + {_mK_2}f_2 \qquad\qquad 6.14$$

where the suffixes 1, 2 and 12 refer to solvent, solute and solution. f_1 and f_2 are molar fractions.

$_mK_{12}$ is calculated from experimental data according to the formula:

$$_mK_{12} = \frac{6\lambda\, n_{12} B_{12}\, M_{12}}{(n_{12}^2 + 2)^2(\epsilon_{12} + 2)^2 d_{12}} \qquad\qquad 6.15$$

for $_mK_1$ the same formula applies but with suffixes 1 instead of 12.

If now $_mK_2$ is calculated from eq. 6.14 the results obtained by several authors show that the values scatter such that the applicability of this method has been questioned (Stuart, 1952, p. 430). Therefore Le Fèvre and Le Fèvre (1955, p. 281) have suggested a somewhat different procedure. First the quantities B, ϵ, d and n which are the direct results of measurements on dilute solutions are smoothed as linear, or when necessary, parabolic functions of f_2:

$$\epsilon_{12} = \epsilon_1(1 + \xi f_2 + \ldots) \qquad\qquad 6.16$$

$$d_{12} = d_1(1 + \eta f_2 + \ldots) \qquad\qquad 6.17$$

$$n_{12} = n_1(1 + \zeta f_2 + \ldots) \qquad\qquad 6.18$$

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$$B_{12} = B_1(1 + \kappa f_2 + \ldots) \qquad\qquad 6.19$$

Inserting these expressions in eq. 6.15 leads to:

$$\infty(_mK_2) = \left[\frac{M_2}{M_1} - \eta + \zeta + \kappa - H\zeta - J\xi\epsilon_1\right]_m K_1 \qquad\qquad 6.20$$

where:

$$H = 4\,\frac{n_1^2}{n_1^2 + 2} \qquad J = \frac{2}{\epsilon_1 + 2}$$

M_1 and M_2 are the molecular weights for the solvent and solute.
For a gas it follows from eq. 6.4, 6.5, and 6.9:

$$_mK = \frac{2\pi N_A}{9}\,(\theta_1 + \theta_2) \qquad\qquad 6.21$$

It is assumed that for $\infty(_mK_2)$ the same formula holds especially
if the solvent has a low Kerr effect and consists of molecules
which presumably have no specific interaction with the solute
(e.g. CCl_4). From the formulae 6.10 and 6.11 for θ_1 and θ_2 it
follows that the molecular Kerr constant depends on six unknown
quantities, the three principal polarizabilities and the three
components of the dipole moment with respect to the axes of the
polarizability ellipsoid. Measurements of the dielectric constant
give the absolute value of the dipole moment. Very often it is
possible to make a reasonable guess as to the direction of the
dipole moment with respect to the principal axes of polarizabi-
lity. For example the dipole moment of thiophene will un-
doubtedly lie along one of these axes. Even in these favourable
cases there remain three unknown quantities α_1, α_2 and α_3.
Therefore two other equations are required to determine the three
principal polarizabilities. One of these equations is obtained
by measurement of the molar refraction, which gives a value of
the mean polarizability:

$$\alpha = \frac{1}{3}\,(\alpha_1 + \alpha_2 + \alpha_3) \qquad\qquad 6.22$$

Measurement of Rayleigh scattering yields a value of θ_1 which

supplies the third equation (Le Fèvre and Purnachandra Rao, 1957; Vuks and Elminov, 1953). Since it is difficult to measure the Rayleigh scattering of solutions accurately and since the interpretation is still uncertain, a different method suggested by Le Fèvre and Le Fèvre (1955, p. 287) may be very helpful. It consists in estimating the polarizabilities by adding bond polarizabilities (i.e. addition of polarizability tensors). This method becomes especially important if the molecules under investigation exist in several conformations. In those cases a knowledge of θ_1, although giving additional information, is still insufficient to determine the occurence of the different steric possibilities.

For the purpose of conformational analysis the procedure consists in calculating for each of the conformations the molecular Kerr constant $_mK$. Both θ_1 and θ_2 are calculated from an estimate of the dipole moment (magnitude as well as direction) and an estimate of the polarizability tensor by the just mentioned additivity rule. If there are not too many conformations and if their $_mK$-values differ notably, it may be possible to decide from the experimental $_mK$ which conformations are the preponderant. Originally the method of addition of bond polarizabilities was introduced by Meyer and Otterbein (1931). This method is justified if the electrons of different bonds do not interact (c.f. Hirschfelder et al., 1954, p. 942). According to Ingold (1953, p. 136) and Le Fèvre and Le Fèvre (1955, p. 300) bond polarizabilities may not always be considered as independent of the rest of the molecule. Electromeric and inductive effects may interfere. Nevertheless it has appeared that the additivity rule leads to satisfactory results, if used in the same class of compounds. We have used bond polarizabilities which were derived by Le Fèvre and Le Fèvre from known Kerr constants and refraction data assuming that the C-H bond is isotropically polarizable.

The dipole moment to be used in the formula for the Kerr constant requires some comments. Le Fèvre and Le Fèvre (1955, p. 285) suggest that the dipole moment should be determined from solutions in the same solvent that is used in measurement of the Kerr constant. For the calculation of the dipole moment we followed the method of Halverstadt and Kumler (1942).

The formulae are:

$$\mu = \sqrt{\frac{9kT}{4\pi N_A}\,(P_d^o - R_D)} \qquad\qquad 6.23$$

where:

$$P_d^o = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\left\{\frac{M_2}{M_1} + M_1\left(\frac{\partial \frac{1}{d}}{\partial f_2}\right)_o\right\} + \frac{3\frac{1}{d_1} \cdot M_1\left(\frac{\partial \epsilon}{\partial f_2}\right)_o}{(\epsilon_1 + 2)^2} \qquad 6.24$$

and

$$R_D = \frac{n_D^2 - 1}{n_D^2 + 2}\,\frac{M}{d} \qquad 6.25$$

for the pure liquid. In the case of the solid m,m'-dianisyl R_D is determined from the solutions by the formula:

$$\infty(R_D) = \frac{n_1^2 - 1}{n_1^2 + 2}\frac{M_2}{d_1} + 6\frac{n_1\left(\frac{\partial n}{\partial f_2}\right)_o}{(n_1^2 + 2)^2}\frac{M_1}{d_1} + \frac{n_1^2 - 1}{n_1^2 + 2}\left(\frac{\partial \frac{1}{d}}{\partial f_2}\right)_o M_1 \qquad 6.26$$

In the following chapters a description of the apparatus will be given (chapter 7) and the results of our measurements on 1-chloro-1-methyl-cyclohexane, anisole, m,m'-dianisyl (3,3'-dimethoxy-biphenyl) and thiophene. At about the same time Le Fèvre et al. also measured the Kerr constants of anisole and thiophene in CCl_4 as solvent. The agreement between their results and ours is satisfactory. In addition to CCl_4 we also used cyclohexane as a solvent for thiophene and benzene as a solvent for 1-chloro-1-methyl-cyclohexane, anisole and m,m'-dianisyl.

The benzene solutions showed a marked solvent effect. The Kerr constants of 1-chloro-1-methyl-cyclohexane measured in CCl_4 and in benzene differed considerably. The same phenomenon was observed with anisole, but not with m,m'-dianisyl. Klages (1952) found similar effects for several polar compounds. The Kerr constants at infinite dilution from benzene solutions was much smaller than those from CCl_4 or heptane solutions. Since these deviations could not be explained with Onsager's internal field Klages concluded to a specific interaction between benzene and the solutes.

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CHAPTER 7

THE APPARATUS

Introduction

Electric birefringence of liquids is measured by a Kerr cell, which consists essentially of a parallel plate condenser. If a potential difference is applied to the plates, the homogeneous electric field makes the medium in the cell double refracting. The cell, then, is optically equivalent to an uniaxial crystalline plate, cut in a direction parallel to its optic axis. The two components of a beam of light, one polarized parallel and the other perpendicular to the electrostatic field, entering the cell with the same phase emerge with a phase difference. The generated retardation is generally quite small and its measurement consti-tutes a difficult problem.

For the determination of such small phase differences several methods are known. They all have in common that light is used which propagates in a direction perpendicular to the static electric field and which is plane polarized at an azimuth of 45°. The beam of light becomes elliptically polarized during its pas-sage through the cell. The methods differ in their way the ellipticity is measured. In the relative methods a second Kerr cell is used to compensate the effect of the first cell. In the absolute methods the ellipticity leaving the Kerr cell is deter-mined. For this purpose a variety of methods is available. We will describe in some detail the two methods which we have used. The first we call the direct method as it is based on the compa-rison of the intensities of the components of the light polarized parallel to the principal axes of the ellips. In the second, the Sénarmont method (1840), the elliptically polarized light is con-verted into linearly polarized light, the plane of polarization of which is rotated with respect to the original azimuth. Al-though the measurements reported were performed in the visual

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part of the spectrum we always used photoelectric methods. This made it possible to extend these measurements also to the ultra-violet part of the spectrum.

The direct method has also been used by Ingersoll (1931) and Benoit (1951). The Sénarmont method is very similar to that described by O'Konski and Zimm (1950). They used a Foucault prism as ¼ λ-plate whereas we used a Soleil-compensator.

In A we describe the experimental arrangement. B gives the discussion on the optical method. C contains some additional remarks.

A. E x p e r i m e n t a l   a r r a n g e m e n t

The arrangement of the apparatus*) is illustrated in fig. 1.
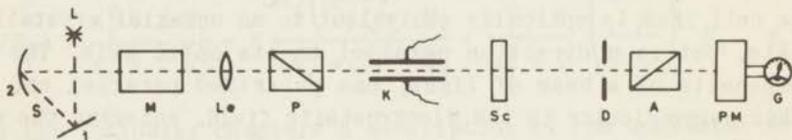
Figure 1. Optical arrangement

L. Highpressure mercury arc (Philips, HPK 125 W, brightness 600 Stilb).
S. Aluminized mirrors.
M. Mirror double monochromator (Kipp, type van Cittert, opening F/6).
Le. Quartz-LiF-achromate (focal length 10 cm.).
P. Polarizer   Glan-Thompson prisms (effective aperture
A. Analyzer   1 x 1 cm².).
K. Kerr cell.
Sc. Soleil-compensator (Steeg und Reuter), adjustable at 1/1000 λ at 546 mμ.
D. Diaphragm (diameter 0.6 cm.).
PM. Photomultiplier (RCA 1P21).
G. Mirror galvanometer (Kipp, type A5, sensitive to $5 \cdot 10^{-11}$ A.).

The photocurrent was measured without amplification. The analyzer was fixed in a graduated circle equipped with a vernier, adjustable to one minute.

The hollow mirror S_2 imaged the light source on the entrance slit of the monochromator. With the collimator the exit slit was focussed on the photomultiplier. All parts at the right of M were

fixed on an optical bench of 2 m. length. This rather long bench
was very convenient in order to eliminate perturbing effects of
reflections in the Kerr cell and in the compensator. For that
purpose the distance between D, A and PM and the other parts of
the apparatus was made as large as possible. Although this arran-
gement does not guarantee an optimal light flux towards the pho-
tomultiplier, the disadvantage of a waste of light energy is
largely counter-balanced by the rejection of undesired reflec-
tions. Since our measurements are made at the very intense green
Hg-line, the remaining light energy was always sufficient for our
purpose. The beam of light was limited in horizontal direction by
the entrance of the Kerr cell (0.4 cm.) and in vertical direction
by D (0.6 cm.).
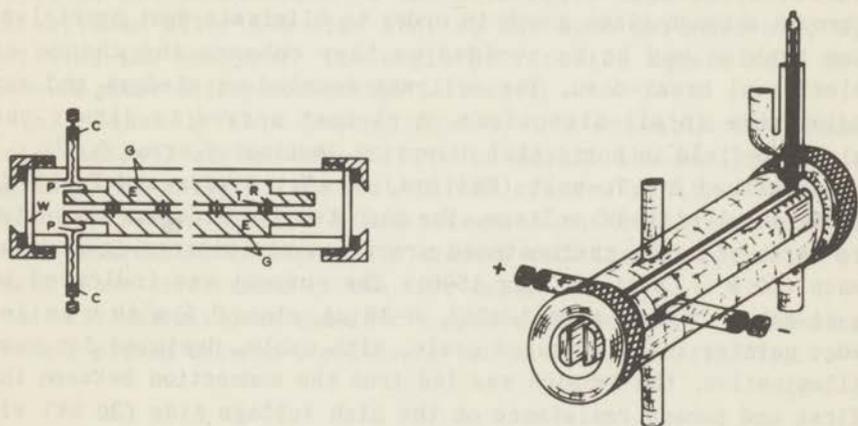
Figure 2.   Kerr cell

Our Kerr cell (fig. 2) was a variant of the one described by Le
Fèvre and Le Fèvre (1953). The electrodes (E), forming a parallel
plate condenser can be thought of to be constructed from a cy-
lindrical brass rod (length 20 cm., diameter 4 cm.) cut along its
axis. They were gilded to avoid corrosion by chemical substances.
The flat sides are kept at a minimal distance by eight glass tubes
(T) of equal length (0.354 cm.). Small glass rods (R) which fit
in holes of the plates keep these glass rings in position. From
the ends the cylindrical sides were fraised over a distance of
4 cm. to make the back flat, so that the correction formula of
Chaumont (1915, 1916) for edge disturbances of the electric field

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could be applied. The condenser fits in a double-walled pyrex
tube (inner diameter 4 cm.). Spacers push the electrodes away
from the wall and keep the plates at the minimal distance. The
pyrex tube was thermostated (25.0^{o}C). Quartz windows (W) were
pressed against the ground flat ends of the glass cylinder and
made a liquid-tight connection. These windows (optically ground
fused silica, diameter 45 mm., thickness 2mm.) showed a small
birefringence (20 minutes). In the description of the optical
method we will discuss its influence. Thin platinum wires (P),
connected to the electrodes, conduct the electric potential
difference through long side arms (length 5 cm.) via liquid-tight
seals to the outer connections of the cell. The cell could be
dismounted for cleaning purposes.

Before filling the cell the liquid (100 cc) was filtered
through a rough glass gooch in order to eliminate dust particles.
Gas bubbles had to be avoided as they enhance the chance of
electrical break-down. The cell was mounted on sledges and was
adjustable in all directions. A plummet served to direct the
electric field in horizontal direction (estimated error 0.5^{o}).

An earthed E.H.T.-unit (Philips, 25 kV.; Siezen and Kerkhof,
1948) supplied the DC voltage. The high tension side was connected
to earth via five thermostated precision resistances in series,
each 500 M Ω (Resista, Rsg 8500). The current was indicated by
a μA-meter (Goerz, type 124217, 0-30 μA, class 0.5) with a knife-
edge pointer and a mirrored scale. With cable, designed for neon
illumination, the tension was led from the connection between the
first and second resistance on the high voltage side (20 kV) via
a switch to the Kerr cell. All sharp edges in the electrical
circuit were avoided and the relative humidity of the room was
kept low (20-30 %) in order to suppress the spraying of the high
tension. The voltage difference on the Kerr cell was measured by
reading the μA-meter and multiplying the current with a constant
resistance which was determined as $1.86 \cdot 10^{9} \Omega$ (error 1.5 %).

The 1P21 photomultiplier was fed with stabilized 1000 V DC. No
absolute measurements of the light intensity were made, since only
relative intensities were needed. To avoid the dependency of the
photocurrent on the plane of polarization of the incident light
(Glancy, 1952) a piece of white type-writer paper, which depola-
rized the light sufficiently, was wrapped around the phototube.
At the green mercury line the waste of light intensity was of no
importance. In order to avoid leakage due to humidity the dynode

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resistances were heated to some degrees above room temperature. As the photocurrent was usually of the order of 10^{-8} A, fatigue effects were negligible. The dark current was about $4 \cdot 10^{-10}$ A. In order to keep the photocurrent constant, the light source as well as the E.H.T.-unit were fed by stabilized power supplies.

B. The determination of the phase difference

I. *The direct photoelectric method (D)*

In this rather simple method the uncharged Kerr cell is placed between two crossed polarizers. The photocurrent, which is minimal in this case, rises to a certain value when a tension is applied to the connections of the Kerr cell. This value is reestablished after the high tension has been switched off, by rotating the analyzer. The angle of rotation equals half the induced phase difference in the Kerr cell.

Unfortunately this method is not very suitable for small retardations, as the sensitivity to adjust the analyzer to a certain intensity is minimal in the crossed position (cf. H. Rudolph, 1955). Another disadvantage is the interference of a small retardation in the quartz windows with the determination of small phase differences in the Kerr cell.

As an illustration we consider a system of two double refracting plates, placed between a polarizer and an analyzer (fig. 3).
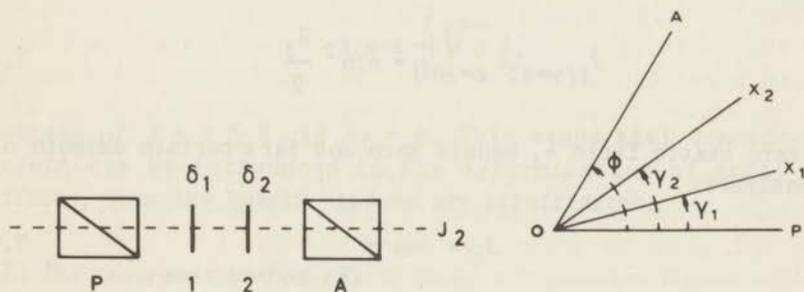
Figure 3.

P and A are the polarizer and the analyzer. OP and OA are the vibration directions of polarizer and analyzer. OX_1, OX_2 are the fast directions of the plates 1 and 2. δ_1, δ_2 are the phase

differences introduced by 1 and 2. ϕ, γ_1, γ_2 are the azimuths of the analyzer and the plates 1 and 2, measured from OP. J_2 is the intensity emerging from the analyzer. According to Jerrard (1938, eq. 4b):

$$J_2 = \cos^2\phi + \sin 2\gamma_1 \cos 2(\phi - \gamma_2)\sin 2(\gamma_2 - \gamma_1) \sin^2 \frac{\delta_1}{2}$$

$$+ \cos 2\gamma_1 \sin 2(\phi - \gamma_2)\sin 2(\gamma_2 - \gamma_1)\sin^2 \frac{\delta_2}{2}$$

$$+ \sin 2\gamma_1 \sin 2(\phi - \gamma_2)\cos^2(\gamma_2 - \gamma_1)\sin^2 \frac{(\delta_1 + \delta_2)}{2}$$

$$- \sin 2\gamma_1 \sin 2(\phi - \gamma_2)\sin^2(\gamma_2 - \gamma_1)\sin^2 \frac{(\delta_1 - \delta_2)}{2} \qquad 7.1$$

where the intensity emerging from the polarizer is assumed to be 1. If we have only one plate: $\gamma_2 = \delta_2 = 0$ and

$$J_1 = \cos^2\phi + \sin 2\gamma_1 \sin 2(\phi - \gamma_1)\sin^2 \frac{\delta_1}{2} \qquad 7.2$$

The direct photoelectric method consists of one retardation plate (Kerr cell) at azimuth $\gamma_1 = 45°$ and crossed polarizers. Therefore:

$$J_{1(\gamma = 45° \ \phi = 90°)} = \sin^2 \frac{\delta_1}{2} \qquad 7.3$$

With zero static field δ_1 equals zero and for a certain azimuth of the analyzer:

$$J_o = \cos^2\phi \qquad 7.4$$

When J_1 from eq. 7.3 is equal to J_o of 7.4, the difference of ϕ from the crossed position equals half the phase difference of the Kerr cell.

To discuss the influence of a birefringent window let us assume that the false retardation (δ_2) can be described with an extra plate of the same azimuth as the Kerr cell. We consider δ_2 to be

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so small that $\sin\delta_2 \cong \delta_2$ and $\cos\delta_2 \cong 1$. In addition we assume that $\sin\delta_1 \cong \delta_1$ and $\cos\delta_1 \cong 1$.
The intensity with crossed polarizers is now:

$$J_2 = \frac{1}{4} (\delta_1 + \delta_2)^2 \qquad\qquad 7.5$$

After the high tension on the Kerr cell has been switched off, the intensity reaching the photomultiplier is (see eq. 7.2):

$$J_1 = \cos^2\phi - \frac{\delta_2^2}{4} \cos2\phi \qquad\qquad 7.6$$

Let $\chi = 90° - \phi$, then:

$$J_1 = \sin^2\chi + \frac{\delta_2^2}{4} \cos2\chi \qquad\qquad 7.7$$

Equalizing J_2 (eq. 7.5) and J_1 (eq. 7.7) and assuming that $\sin\chi \cong \chi$ and $\cos2\chi \cong 1$:

$$\frac{1}{4} (\delta_1 + \delta_2)^2 = \chi^2 + \frac{\delta_2^2}{4} \qquad\qquad 7.8$$

Assuming as an example, $\delta_2 = \delta_1$:

$$\chi = \pm \frac{1}{2}\sqrt{3}\,\delta_1 \qquad\qquad 7.9$$

instead of $\chi = \pm \frac{1}{2}\delta_1$ if $\delta_2 = 0$. This means that considerable errors can be introduced in the determination of small Kerr effects, when the quartz windows are birefringent.

II. *The Sénarmont method (S)*
   In the Sénarmont method a ¼-wave plate (with azimuth 0°) is used to convert the elliptically polarized light emerging from the Kerr cell in a linearly polarized one. Combined, the Kerr cell and the Soleil-compensator act as a rotator of the plane of polarization. The angle over which the plane is rotated equals half the phase difference in the Kerr cell.

This is illustrated by substituting in eq. 7.1: $\gamma_1 = 45°$, $\gamma_2 = 0°$, $\delta_2 = 90°$. Then:

$$J_2 = \cos^2\phi - \cos 2\phi \sin^2\frac{\delta_1}{2} + \frac{1}{2}\sin 2\phi\left\{\sin^2\left(\frac{\delta_1}{2} + 45°\right) - \right.$$
$$\left. \sin^2\left(\frac{\delta_1}{2} - 45°\right)\right\} \qquad 7.10$$

Or

$$J_2 = \cos^2\left(\phi - \frac{\delta_1}{2}\right) \qquad 7.11$$

Or

$$J_2 = \sin^2\left(\chi + \frac{\delta_1}{2}\right) \qquad 7.12$$

where $\chi = 90° - \phi$

Evidently for $\chi = \frac{-\delta_1}{2}$, $J_2 = 0$.

Now the influence of birefringent windows has to be considered. A birefringent plate before the Kerr cell with an azimuth of $0°$ or $45°$ does not change the angle difference of the minimum of light intensity with and without static electric field. Neither would the exit window show any change when its azimuth is $45°$.

We will show, however, that this does not apply when the azimuth is $0°$. This situation is equivalent to the case that the ¼-wave plate has not an exact phase difference of $90°$. Now we have to substitute in 7.1: $\gamma_1 = 45°$, $\gamma_2 = 0°$, $\delta_2 = 90° + \rho$.
Then:

$$J_2 = \cos^2\phi - \cos 2\phi \sin^2\frac{\delta_1}{2} + \frac{1}{2}\sin 2\phi\left[\sin^2\left\{\frac{1}{2}(\delta_1 + \rho) + 45°\right\} \right.$$
$$\left. -\sin^2\left\{\frac{1}{2}(\delta_1 - \rho) - 45°\right\}\right] \qquad 7.13$$

Or

$$J_2 = \cos^2\left(\phi - \frac{\delta_1}{2}\right) - \sin 2\phi \sin \delta \sin^2\frac{\rho}{2} \qquad 7.14$$

For estimating the minimum value of J_2, $\dfrac{\partial J_2}{\partial \phi} = 0$. Or:

$$\sin 2\phi \cos \delta_1 = \cos 2\phi \sin \delta_1 \cos \rho \qquad 7.15$$

giving

$$\tan 2\phi = \tan \delta_1 \cos \rho \qquad 7.16$$

Introducing $\chi = 90° - \phi$:

$$\tan 2\chi = -\tan \delta_1 \cos \rho \qquad 7.17$$

Suppose now that $\tan 2\chi \cong 2\chi$ and $\tan \delta_1 \cong \delta_1$
then: $2\chi = -\delta_1 \cos \rho$
In this case ρ may be as large as $8°$ before an error of only 1%
is made. This result indicates that the influence of the bire-
fringence of the quartz windows is negligible in the Sénarmont
method.

Similarly it can be shown that the azimuths of the Kerr cell
and the Soleil-compensator could be adjusted sufficiently pre-
cise to keep the error in the final determination of the retar-
dation in the Kerr cell far below 1%. The same applies to the
quality of the compensator. The Kerr cell could be adjusted
within $0.5°$, the compensator even better.

The method of symmetrical angles (H. Rudolph, 1955) was used to
determine the azimuth of the plane of polarization of the beam
emerging from the compensator. We chose a symmetrical angle of
$2°$ to $3°$ to combine the sensitivity of the optical method with
that of the photoelectric system.

C. The performance of the apparatus

As to the two polarized lightbeams, according to Kerr's law:

$$\Delta = B l E^2 \qquad 7.18$$

Here Δ is the pathway difference expressed in wave lengths. l is
the length of the effective lightpath (in cm.) through the Kerr
cell, E is the electric field (in e.s.u.). B is the Kerr constant

(in e.s.u.). Both the methods D and S give as a result an angle ϕ equal to half the retardation in the Kerr cell. Consequently $\Delta = \dfrac{\phi}{180}$, where ϕ is expressed in degrees.

The effective lightpath l through the Kerr cell has been calculated by a formula due to Chaumont (1915, 1916), to include edge disturbances of the condensor plates:

$$l = l_o + \frac{a}{\pi}\left[1 + \frac{d}{a}\,{}^e log \left(1 + \frac{a}{d} \right) \right]$$ 7.19

l_o is the length of the plates, a their distance and d their thickness (all in cm.). In our case $l_o = 20.02$ cm., $a = 0.354$ cm., $d = 0.97$ cm. Consequently $l = 20.22$ cm. We estimate the error in l to be certainly less then ½%. $E = \dfrac{V}{a}$, where V is the potential difference between the plates (in e.s.u.). $V = \dfrac{R \cdot x}{300}$, where R is 1862MΩ and x is the current (in μA) through R. Consequently $E = \dfrac{1862}{300} \cdot \dfrac{x}{0.354}$

and $B = \dfrac{\phi}{x^2}\, 0.895 \cdot 10^{-6}$ e.s.u..

For estimating the accuracy of the determination of B, we list the following relative errors: resistance 1.5 %, current 0.5 %, length of the Kerr cell 0.5 %, phase difference ϕ about 1 minute for the method S and 2 to 3 minutes for method D. The relative error in the determination of Δ depends on its absolute value, but for the values occuring in our experiments it is about 1 %. Altogether the relative error in B is about 5 % or in some unfavourable cases of very low B-values perhaps 10 %.

The internal consistency of our measurements, however, is much better since errors in the high resistance and in the lightpath of the Kerr cell remain constant. From the evaluation of our measurements by the method of least squares it follows that the standard deviations of B-determinations are in the range of ½ - 3 %.

Since the main sources of errors are to be sought in the measurements of the azimuth of the analyzer and of the current through the resistance, the accuracy of the measurements can be improved by using better devices for the determination of these quantities. For instance a Faraday cell has to be preferred to an analyzer with mechanical adjustment.

CHAPTER 8

MEASUREMENTS AND THEIR EVALUATION

A. R e l i a b i l i t y   o f   t h e   a p p a r a t u s

In order to check the reproducibility of the measurements with our Kerr apparatus we determined the Kerr constants B for the pure solvents CCl_4, C_6H_6 and C_6H_{12}. With each solvent a number of determinations were performed, sometimes using the direct method sometimes the Sénarmont method. The results are given in table A. Brackets and asterisks indicate that the samples were taken from the same batch of destillate.

	CCl_4		C_6H_6		C_6H_{12}
	Method D	Method S	Method D	Method S	Method S
	$B.10^8$	$B.10^8$	$B.10^8$	$B.10^8$	$B.10^8$
	⎧ 0.77	⎧ 0.88	⎧ 4.25	⎧ 4.21	⎧ 0.63
	⎩ 0.84	⎩ 0.87	⎩ 4.27	⎩ 4.22	⎩ 0.59
	⎧ 1.17	⎧ 0.89	⎧ 4.24	4.19*	⎧ 0.61
	⎩ 1.08	⎩ 0.89	⎩ 4.24		⎩ 0.57
		⎧ 0.92	⎧ 4.14		
		⎩ 0.90	⎩ 4.13		
		⎧ 0.86	4.20*		
		⎩ 0.85			
		⎧ 0.85			
		⎩ 0.85			
Mean value	0.97	0.876 ± 0.008	4.21 ± 0.02	4.21	0.60

Table A

From inspection of these results it becomes clear that method S is superior to method D. Probably the main reason for the lower reproducibility of method D is its higher sensitivity to the birefringence of the Kerr cell windows. These had to be removed for cleaning the cell when changing from one batch to an other. The birefringence of the Kerr cell windows was about $20'$, whereas the birefringence of a CCl_4 filling was about $100'$. With benzene this amounted to $520'$. This explains why the reproducibility of method D is worse with CCl_4 than with C_6H_6. As has been discussed in chapter 7 the Sénarmont method is largely independent of the birefringence of the quartz windows. Another advantage of the Sénarmont method is that with small retardations more light is available than in the direct method.

In order to compare our results with those given in litterature, some values are collected in table B, all pertaining to the green mercury line (546 mμ) and to $20°C$.

	C_6H_6	CCl_4
	$B.10^8$	$B.10^8$
Briegleb (1931)	4.08	0.714
Dillon (see Briegleb)	4.17	-
Leiser (see Briegleb)	4.52	0.884
Stuart and Volkmann (1933)	4.03	0.842
Otterbein (1934)	-	0.84
Le Fèvre and Le Fèvre (1953)[*]	4.71	0.76
Our results[**]	4.24	0.88

Table B

The standard deviation of our CCl_4 value is 0.008, that of a single measurement 0.024. For benzene the standard deviations are 0.02 and 0.05. It is seen that our values lie in the same range as those given by others.

Since the electric birefringence of CS_2 has been measured many

[*] The dispersion law of Havelock was applied for wave length's corrections.
[**] For the temperature corrections data quoted by Stuart and Volkmann (1933) were used.

times and since its Kerr constant is the most accurate known, we also measured this quantity. With the direct photoelectric method we found: $B = (34.35 \pm 0.04) \cdot 10^{-8}$. By means of the Soleil-compensator (used as a real compensator) we found: $B = (34.64 \pm 0.07) \cdot 10^{-8}$. International Critical Tables gives: $B = 34.88 \cdot 10^{-8}$. In all cases the wave length of the light was 546 mμ and the temperature 25°C.

In addition to Kerr constants dielectric constants, refractive indices and densities were measured. For the dielectric constant measurements the commercial "WTW Dipolmeter" (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) was used. Density measurements were performed with pyknometers with a volume of 6cc. (for a description see Scholte and de Vos, 1953). The refractive indices were measured with a refractometer of the Abbe type*) (Bausch and Lomb precision refractometer, type 33.45.03).

The quantities B, ϵ, n_D, n_{Hg} (Hg refers to 546 mμ), d and the specific volume $v = \frac{1}{d}$ were determined for a series of concentrations. The concentrations are given in molar fractions. For each quantity the method of least squares was used to find the best parabola to fit the experimental points. All the measurements have been given the same weight factor. The concentrations were considered to be known exactly.

B. Chemicals

I. Solvents

Benzene (Merck, A.R.) and cyclohexane (Fluka, benzene-free, puriss. F 4° - 5,5°C) were refluxed over Na and fractionated with a Widmer column. CCl_4 (Merck, A.R.) was refluxed over P_2O_5 and also fractionated. A fresh batch of 1.8 l. was prepared for each series of measurements.

II. 1-Chloro-1-methyl-cyclohexane

1-Chloro-1-methyl-cyclohexane was prepared**) by HCl-solvolysis of the corresponding alcohol (cf. Brown and Fletcher, 1959). 1 mole of the alcohol was shaken vigorously with 5 moles of con-

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*) The measurements were performed with a refractometer that was placed at our disposal by the department "Fysische Chemie II".
**) I am particularly indebted to Mr. H.M. van Dort for the preparation of this compound and for the help in performing the measurements described in this thesis.

centrated HCl at a temperature of $0°C$. After separating the two layers, the upper layer was dissolved in ether and treated with a diluted $NaHCO_3$ solution, then washed with water and dried over $MgSO_4$. Next the ether was distilled off and the remaining compound was distilled in vacuo. The liquid was stored at $-15°C$ with a small amount of P_2O_5 as a desiccant.

Before the measurements were made, the compound was redistilled. The boiling point appeared not to have changed during storage. Although the pure liquid liberated HCl easily at room temperature, the dilute solutions of the compound proved to remain unaltered during the measurements. B.p. $38.5°C$ at 14 mm.. $n_{Hg}^{25} = 1.4577$. $n_D^{25} = 1.4557$, $d_4^{25} = 0.9668$ giving $R_D = 37.27$ cc./mol.

According to Mousseron et al. (1946):
$n_D^{25} = 1.4565$, $d_4^{25} = 0.965$ giving $R_D = 37.39$ cc./mol.

According to Van der Bij and Kooyman (1952):
$n_D^{20} = 1.4579$, $d_4^{20} = 0.9665$ giving $R_D = 37.44$ cc./mol.

III. *Anisole*

Anisole (Fluka, purum) was shaken with a 10% NaOH-solution to remove any possible phenol. It was dried over $CaCl_2$ and distilled (b.p. $51° - 52°C$ at 15 mm.). The refractive index was $n_D^{25} = 1.5146$, whereas the value given in Weissberger (Organic Solvents) is $n_D^{25} = 1.5143$.

IV. *m,m'-Dianisyl (3,3'-dimethoxy-biphenyl)*

m,m'-Dianisyl (available at the laboratory) was recrystallized from ethanol until constant melting point ($42° - 43.5°C$)(cf. Adams and Kornblum, 1941).

V. *Thiophene*

Thiophene (Fluka, purum) was dried over Na and distilled before the measurements were made. $n_D^{25} = 1.5254$ whereas Weissberger (Organic Solvents) gives 1.5257.

C. Measurements

In the following tables we report the observed data of B, ϵ, d and n_{Hg} for each series of measurements and n_D for m,m'-dianisyl. Moreover the constants are given of the best parabolic curves

$y = A + Bf_2 + Cf_2^2$, which represent the mentioned quantities as functions of the concentrations. S_A, S_B, S_C and S are the standard deviations of A, B, C and of a single measurement*). All experiments were performed at $25°C$. B and n_{Hg} were determined at a wave length of light of 546 mμ. For controll we determined all quantities of the pure solvent on two different samples, one at the beginning of each series, the other at the end.

1-Chloro-1-methyl-cyclohexane in CCl$_4$. Method D.

$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v
0	1.17	1.5844	2.2310	1.45965	0.63115
0	1.08	1.5844	2.2310	1.45965	0.63115
5.850	1.35	1.5794	2.2637	1.45968	0.63315
8.568	1.48	1.5770	2.2779	1.45968	0.63412
21.889	2.01	1.5657	2.3534	1.45977	0.63869
27.411	2.22	1.5611	2.3854	1.45982	0.64057
37.154	2.63	1.5529	2.4426	1.45985	0.64396
55.940	3.49	1.5378	2.5479	1.45988	0.65028
115.53	6.35	1.4907	2.8717	1.46004	0.67083

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	1.126	0.016	38.880	0.916	54.969	7.833	0.029
d	1.58437	0.00005	-0.859	0.003	0.420	0.027	0.00010
ϵ	2.2300	0.0007	5.757	0.042	-1.733	0.362	0.0014
n_{Hg}	1.45965	0.00001	0.0058	0.0006	-0.021	0.005	0.00002
v	0.63116	0.00002	0.343	0.001	0.004	0.011	0.00004

Table C

1-Chloro-1-methyl-cyclohexane in CCl_4. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	0.881	1.5844	2.2300	1.45955	0.63115	
	0	0.874	1.5844	2.2334	1.45955	0.63115	
	8.066	1.188	1.5775	2.2768	1.45956	0.63391	
	22.714	1.764	1.5650	2.3629	1.45964	0.63898	
	34.524	2.280	1.5550	2.4335	1.45969	0.64309	
	51.466	2.979	1.5410	2.5359	1.45978	0.64893	
	66.979	3.681	1.5283	2.6342	1.45978	0.65432	
	101.93	5.363	1.4997	2.8527	1.45993	0.66680	
	115.31	6.123	1.4899	2.9328	1.45994	0.67119	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.883	0.013	37.241	0.647	69.10	5.61	0.022
d	1.5844	0.00013	-0.864	0.006	0.361	0.056	0.00022
ϵ	2.2306	0.0014	5.829	0.068	2.446	0.588	0.0023
n_{Hg}	1.45954	0.000012	0.0046	0.0006	-0.0090	0.0053	0.00002
v	0.63114	0.00006	0.345	0.003	0.032	0.025	0.00010

Table D

1-Chloro-1-methyl-cyclohexane in C_6H_6. Method D.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	4.253	0.8733	2.2648	1.50183	1.1451	
	0	4.274	0.8733	2.2646	1.50182	1.1451	
	3.138	4.230	0.8737	2.2858	1.50159	1.1445	
	6.399	4.275	0.8741	2.3034	1.50130	1.1440	
	15.931	4.333	0.8753	2.3573	1.50062	1.1425	
	23.046	4.367	0.8763	2.4018	1.50014	1.1412	
	28.760	4.446	0.8771	2.4359	1.49971	1.1401	
	49.662	4.622	0.8799	2.5611	1.49821	1.1365	
	71.761	4.918	0.8828	2.6941	1.49674	1.1328	

	A	S_A	B	S_B	C	S_C	S
$b \cdot 10^8$	4.249	0.011	3.913	0.953	75.146	13.58	0.020
d	0.87328	0.00002	0.131	0.002	0.026	0.029	0.00004
ϵ	2.2653	0.0007	5.879	0.061	1.377	0.863	0.0013
n_{Hg}	1.50182	0.000013	-0.0755	0.0012	0.065	0.016	0.000024
v	1.14510	0.00004	-0.172	0.004	-0.004	0.052	0.00008

Table E

1-Chloro-1-methyl-cyclohexane in C_6H_6. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	4.208	0.8731	2.2692	1.50160	1.1453	
	0	4.219	0.8731	2.2692	1.50159	1.1453	
	7.817	4.262	0.8742	2.3165	1.50101	1.1439	
	16.946	4.324	0.8754	2.3688	1.50028	1.1423	
	24.803	4.416	0.8764	2.4163	1.49971	1.1410	
	38.791	4.513	0.8782	2.4990	1.49866	1.1387	
	48.263	4.588	0.8795	2.5564	1.49810	1.1370	
	71.913	4.936	0.8825	2.6982	1.49645	1.1331	
	98.221	5.371	0.8858	2.8531	1.49467	1.1289	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	4.219	0.011	4.901	0.644	69.27	6.68	0.019
d	0.87312	0.00002	0.134	0.001	-0.052	0.011	0.00003
ϵ	2.2691	0.0005	5.943	0.030	0.088	0.315	0.0009
n_{Hg}	1.50159	0.000024	-0.0764	0.0014	0.063	0.015	0.000041
v	1.14529	0.000026	-0.175	0.0015	0.083	0.015	0.000043

Table F

Anisole in CCl_4. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	0.856	1.5844	2.2326	1.45985	0.63115	
	0	0.847	1.5844	2.2327	1.45987	0.63115	
	5.111	0.949	1.5810	2.2434	1.46018	0.63251	
	9.944	1.075	1.5777	2.2529	1.46055	0.63383	
	24.017	1.370	1.5685	2.2804	1.46157	0.63755	
	34.543	1.555	1.5614	2.3053	1.46237	0.64045	
	45.549	1.767	1.5541	2.3274	1.46318	0.64346	
	50.431	1.893	1.5510	2.3376	1.46355	0.64475	
	57.367	1.989	1.5463	2.3511	1.46404	0.64671	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.850	0.009	22.077	0.944	-36.65	16.93	0.015
d	1.58439	0.00004	-0.666	0.004	0.093	0.071	0.00006
ϵ	2.2326	0.0006	2.053	0.061	0.439	1.096	0.0010
n_{Hg}	1.45984	0.000014	0.0715	0.0014	0.034	0.026	0.000023
v	0.631155	0.000015	0.265	0.0010	0.102	0.028	0.000025

Table G

Anisole in CCl_4. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	0.847	1.5840	2.2354	1.45949	0.63131	
	0	0.849	1.5840	2.2353	1.45949	0.63131	
	6.315	0.977	1.5799	2.2476	1.46001	0.63295	
	14.747	1.117	1.5743	2.2651	1.46059	0.63520	
	24.521	1.361	1.5677	2.2855	1.46137	0.63788	
	34.209	1.529	1.5612	2.3077	1.46208	0.64053	
	42.429	1.689	1.5560	2.3235	1.46260	0.64267	
	53.318	1.902	1.5487	2.3450	1.46338	0.64570	
	63.610	2.092	1.5422	2.3675	1.46416	0.64842	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.845	0.009	20.514	0.766	-13.74	12.38	0.014
d	1.58405	0.00006	-0.671	0.005	0.195	0.085	0.00010
ϵ	2.2350	0.0005	2.085	0.045	-0.083	0.734	0.0009
n_{Hg}	1.45950	0.000022	0.0764	0.0019	-0.056	0.031	0.000036
v	0.63129	0.000025	0.268	0.002	0.031	0.035	0.000041

Table H

Anisole in C_6H_6. Method D.

	$f_2 \cdot 10^3$	$b \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	4.240	0.8732	2.2696	1.50179	1.1452	
	0	4.240	0.8732	2.2668	1.50180	1.1452	
	4.038	4.233	0.8738	2.2741	1.50189	1.1444	
	7.462	4.290	0.8742	2.2796	1.50200	1.1439	
	19.549	4.411	0.8760	2.3115	1.50226	1.1416	
	28.597	4.535	0.8773	2.3281	1.50242	1.1399	
	35.260	4.529	0.8782	2.3416	1.50252	1.1387	
	56.008	4.742	0.8811	2.3893	1.50301	1.1349	
	85.459	5.005	0.8852	2.4517	1.50365	1.1297	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	4.227	0.014	9.511	0.987	-4.86	11.84	0.025
d	0.87319	0.00002	0.143	0.0013	-0.035	0.016	0.00003
ϵ	2.2667	0.0013	2.157	0.089	0.14	1.07	0.0023
n_{Hg}	1.50181	0.000016	0.0211	0.0011	0.004	0.013	0.000028
v	1.14521	0.000025	-0.187	0.002	0.065	0.021	0.000045

Table I

m,m′-Dianisyl in CCl$_4$. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	n_D	v
	0	0.885	1.5846	2.2309	1.45963	1.45731	0.63107
	0	0.890	1.5845	2.2309	1.45967	1.45734	0.63111
	3.158	1.266	1.5818	2.2441	1.46069	1.45839	0.63219
	5.646	1.608	1.5794	2.2554	1.46146	1.45913	0.63315
	6.868	1.782	1.5785	2.2618	1.46188	1.45950	0.63351
	8.513	1.972	1.5771	2.2681	1.46239	1.46002	0.63408
	9.973	2.143	1.5759	2.2744	1.46284	1.46048	0.63456
	13.654	2.689	1.5725	2.2943	1.46403	1.46163	0.63593
	17.198	3.163	1.5696	2.3111	1.46514	1.46270	0.63710
	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.886	0.012	123.54	3.35	531.4	196.6	0.018
d	1.58455	0.00007	-0.890	0.019	1.14	1.11	0.00010
ϵ	2.2309	0.0005	4.165	0.133	30.07	7.80	0.0007
n_{Hg}	1.45965	0.000013	0.324	0.004	-0.288	0.216	0.000020
n_D	1.457335	0.000017	0.321	0.005	-0.543	0.273	0.000025
v	0.63109	0.00003	0.364	0.007	-0.336	0.436	0.00004

Table J

m,m′-Dianisyl in CCl$_4$. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	n_D	v
	0	0.917	1.5842	2.2312	1.45959	1.45728	0.63123
	0	0.904	1.5842	2.2312	1.45959	1.45729	0.63123
	2.234	1.145	1.5824	2.2413	1.46027	1.45794	0.63195
	4.958	1.498	1.5800	2.2525	1.46118	1.45885	0.63291
	6.387	1.656	1.5789	2.2591	1.46160	1.45922	0.63335
	8.510	1.937	1.5768	2.2694	1.46231	1.45994	0.63420
	11.194	2.258	1.5745	2.2815	1.46323	1.46085	0.63512
	13.515	2.559	1.5725	2.2946	1.46399	1.46157	0.63593
	15.369	2.771	1.5717	2.2980	1.46430	1.46190	0.63625
	A	S_A	b	S_B	C	S_C	S
$B \cdot 10^8$	0.903	0.009	117.53	3.08	307.3	202.1	0.014
d	1.5843	0.00015	-0.907	0.052	4.34	3.42	0.00024
ϵ	2.2310	0.0010	4.525	0.329	-2.0	21.6	0.0015
n_{Hg}	1.45956	0.00005	0.336	0.018	-1.34	1.19	0.00008
n_D	1.45726	0.00005	0.326	0.018	-1.13	1.15	0.00008
v	0.63119	0.00006	0.363	0.021	-1.63	1.39	0.00010

Table K

m, m'-Dianisyl in C_6H_6. Method D.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	n_D	v
	0	4.137	0.8730	2.2687	1.50190	1.49789	1.1455
	0	4.130	0.8730	2.2692	1.50189	1.49788	1.1455
	1.469	4.327	0.8738	2.2760	1.50226	1.49823	1.1444
	3.797	4.634	0.8750	2.2892	1.50282	1.49882	1.1429
	6.082	4.873	0.8763	2.3011	1.50337	1.49933	1.1412
	7.841	5.082	0.8772	2.3068	1.50381	1.49978	1.1400
	10.845	5.455	0.8788	2.3179	1.50451	1.50046	1.1379
	15.523	6.252	0.8812	2.3407	1.50559	1.50152	1.1348
	28.164	7.898	0.8877	2.3976	1.50854	1.50442	1.1265

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	4.128	0.033	124.82	6.96	343	247	0.057
d	0.87300	0.000016	0.540	0.003	−0.653	0.120	0.000028
ϵ	2.2697	0.0010	4.731	0.216	−7.25	7.64	0.0018
n_{Hg}	1.501900	0.000008	0.243	0.0018	−0.270	0.064	0.000015
n_D	1.497890	0.000012	0.240	0.0025	−0.299	0.089	0.000021
v	1.14550	0.00003	−0.711	0.006	1.286	0.202	0.00005

Table L

Thiophene in CCl_4. Method D.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v	
	0	0.77	1.5843	2.2435	1.45959	0.63119	
	0	0.84	1.5844	2.2440	1.45960	0.63115	
	17.870	0.90	1.5767	2.2519	1.46068	0.63424	
	39.932	1.08	1.5666	2.2618	1.46216	0.63832	
	68.294	1.28	1.5544	2.2740	1.46396	0.64334	
	137.17	1.79	1.5237	2.3044	1.46822	0.65630	
	188.95	2.13	1.5001	2.3287	1.47155	0.66662	
	219.80	2.31	1.4856	2.3415	1.47359	0.67313	
	240.08	2.48	1.4761	2.3520	1.47496	0.67746	

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.793	0.016	7.325	0.430	−1.451	1.812	0.027
d	1.5843	0.0001	−0.432	0.003	−0.077	0.012	0.0002
ϵ	2.2439	0.0003	0.437	0.008	0.047	0.033	0.0005
n_{Hg}	1.45961	0.00003	0.0622	0.0008	0.006	0.004	0.00005
v	0.6312	0.00005	0.171	0.0013	0.089	0.005	0.00008

Table M

Thiophene in C_6H_{12}. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v
	0	0.626	0.7743	2.0203	1.42571	1.2915
	0	0.589	0.7743	2.0205	1.42570	1.2915
	26.89	0.771	0.7792	2.0310	1.42732	1.2834
	53.77	0.928	0.7843	2.0418	1.42895	1.2750
	72.89	1.014	0.7880	2.0514	1.43022	1.2690
	101.99	1.184	0.7940	2.0666	1.43212	1.2594
	137.45	1.439	0.8012	2.0843	1.43458	1.2481
	163.35	1.628	0.8065	2.0959	1.43642	1.2399
	224.70	2.011	0.8202	2.1268	1.44108	1.2192

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.609	0.013	5.544	0.306	3.291	1.398	0.021
d	0.7743	0.00006	0.182	0.001	0.101	0.006	0.00009
ϵ	2.0198	0.0007	0.429	0.016	0.220	0.074	0.0011
n_{Hg}	1.42571	0.00001	0.0584	0.0003	0.045	0.0012	0.00002
v	1.2916	0.0001	-0.305	0.002	-0.074	0.010	0.0002

Table N

Thiophene in C_6H_{12}. Method S.

	$f_2 \cdot 10^3$	$B \cdot 10^8$	d	ϵ	n_{Hg}	v
	0	0.608	0.7764	2.0209	1.42551	1.2880
	0	0.572	0.7764	2.0200	1.42553	1.2880
	30.77	0.801	0.7821	2.0330	1.42740	1.2786
	55.39	0.946	0.7868	2.0431	1.42902	1.2710
	79.73	1.048	0.7917	2.0529	1.43060	1.2631
	121.04	1.300	0.7999	2.0743	1.43327	1.2502
	146.62	1.505	0.8052	2.0882	1.43510	1.2419
	180.20	1.712	0.8126	2.1036	1.43759	1.2306
	212.49	1.943	0.8197	2.1191	1.44004	1.2200

	A	S_A	B	S_B	C	S_C	S
$B \cdot 10^8$	0.610	0.015	5.574	0.385	3.390	1.844	0.024
d	0.7764	0.00005	0.182	0.001	0.101	0.006	0.00007
ϵ	2.0201	0.0008	0.411	0.019	0.279	0.092	0.0012
n_{Hg}	1.42554	0.00003	0.0596	0.0008	0.040	0.004	0.00005
v	1.2880	0.00008	-0.304	0.002	-0.077	0.009	0.00012

Table O

CHAPTER 9

DISCUSSION OF RESULTS

A. 1-Chloro-1-methyl-cyclohexane

Solvent	Calc. from table	$\infty(_mK_2) \cdot 10^{12}$	$\mu(D)$
CCl_4	C	56.9 ± 1.4	2.16 ± 0.01
CCl_4	D	54.8 ± 1.0	2.18 ± 0.01
C_6H_6	E	-1.3 ± 1.3	2.10 ± 0.01
C_6H_6	F	-0.1 ± 0.9	2.11 ± 0.01

Table P

The $_mK$-values with CCl_4 as solvent agree satisfactorily. The same is true if benzene is used as a solvent. It is surprising, however, that the Kerr constants in the two solvents are entirely different.

Conformational analysis

When we assume that 1-chloro-1-methyl-cyclohexane is completely in the chair form, the question remains whether the chloro atom is more favoured in the equatorial than in the axial position. In order to contribute to the solution of this problem we will estimate the Kerr constants of the two possible chair conformations. The estimates are based on the empirical rule that the polarizability tensor of the molecule can be obtained as a sum of the polarizability tensors of the bonds. Moreover it will be assumed that the Kerr constants are determined by the dipole orientation term only, the anisotropic polarizability term being generally small for compounds with a relatively large dipole

moment. The dipole moment of 1-chloro-1-methyl-cyclohexane is assumed to lie along the direction of the C-Cl bond. Taking the 1-axis parallel to the dipole moment the formulae to be used are:

$$_\infty(_mK_2) = \frac{2\pi}{9} N_A \theta_2 \qquad\qquad 9.1$$

where

$$\theta_2 = \frac{\mu^2}{45k^2T^2} (2b_{11} - b_{22} - b_{33}) \qquad\qquad 9.2$$

In the calculations we have used the bond polarizabilities given by Le Fèvre and Le Fèvre (1956). In their system it is assumed that the C-H bond is isotropically polarizable whereas the polarizabilities of the other bonds have rotational symmetry around the link. From their data we quote:

$$10^{23}b_l^{C-Cl} = 0.382 \quad cc.; \qquad 10^{23}b_t^{C-Cl} = 0.185 \quad cc.$$
$$10^{23}b_l^{C-C} = 0.0986 \quad cc.; \qquad 10^{23}b_t^{C-C} = 0.0274 \quad cc.$$
$$10^{23}b_l^{C-H} = 0.0635 \quad cc.$$

l refers to longitudinal, t to transversal.

As far as we could determine, the b values have been derived from Kerr constants and depolarization factors at the Na D-line and refraction data at infinite wave length. This should be kept in mind when comparing values calculated with these constants, with experimental data.

The coordinate axes are chosen such that the 1-axis is in the C-Cl direction and the 2-axis in the H_3C-C-Cl plane.

$_\infty(_mK_2)$ for equatorial Cl
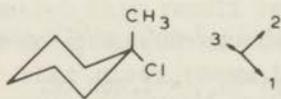
Figure 4

$$b_{11} = b_l^{C-Cl} + 2b_l^{C-C} + 5b_l^{C-C} \sin^2 19°28' + 5b_t^{C-C} \cos^2 19°28' + 13b_l^{C-H}$$

$$b_{22} = b_t^{C-Cl} + 2b_t^{C-C} + 4b_l^{C-C} \cos^2 19°28' \cos^2 60° + b_l^{C-C} \cos^2 19°28' +$$

$$+ 4b_t^{C-C} \sin^2 19°28' \cos^2 60° + 4b_t^{C-C} \sin^2 60° +$$

$$+ b_t^{C-C} \sin^2 19°28' + 13b_l^{C-H}$$

$$b_{33} = b_t^{C-Cl} + 2b_t^{C-C} + 4b_l^{C-C} \cos^2 19°28' \sin^2 60° +$$

$$+ 4b_t^{C-C} \sin^2 19°28' \sin^2 60° + 4b_t^{C-C} \cos^2 60° + b_t^{C-C} + 13b_l^{C-H}$$

$$10^{23}b_{11} = 1.581 \text{ cc.}$$
$$10^{23}b_{22} = 1.329 \text{ cc.}$$
$$10^{23}b_{33} = 1.392 \text{ cc.}$$

For $\mu = 2.14$ D and $T = 298°$: $_\infty(_mK_2) = 113 \cdot 10^{-12}$

$_\infty(_mK_2)$ f o r   a x i a l   C l
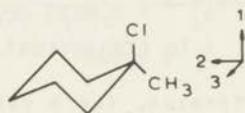
Figure 5

$$b_{11} = b_l^{C-Cl} + 7b_l^{C-C} \sin^2 19°28' + 7b_t^{C-C} \cos^2 19°28' + 13b_l^{C-H}$$

$$b_{22} = b_t^{C-Cl} + 3b_l^{C-C} \cos^2 19°28' + 4b_l^{C-C} \cos^2 19°28' \cos^2 60° +$$

$$+ 4b_t^{C-C} \sin^2 19°28' \cos^2 60° + 4b_t^{C-C} \sin^2 60° +$$

$$+ 3b_t^{C-C} \sin^2 19°28' + 13b_l^{C-h}$$

$$b_{33} = b_t^{C-Cl} + 3b_t^{C-C} + 4b_l^{C-C} \cos^2 19°28' \sin^2 60° +$$

$$+ 4b_t^{C-C} \sin^2 19°28' \sin^2 60° + 4b_t^{C-C} \cos^2 60° + 13b_l^{C-H}$$

$$10^{23}b_{11} = 1.455 \text{ cc.}$$
$$10^{23}b_{22} = 1.456 \text{ cc.}$$
$$10^{23}b_{33} = 1.392 \text{ cc.}$$

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For $\mu = 2.14$ D and $T = 298°$: $_\infty(_mK_2) = 15.9 \cdot 10^{-12}$

Average polarizability

For this substance we found that $\dfrac{b_{11}+b_{22}+b_{33}}{3} = 1.434 \cdot 10^{-23}$ cc.

We determined the refraction at 546 mμ and 589 mμ. The value at infinite wave length was calculated with the extrapolation formula (cf. Böttcher, 1952, p. 256):

$$[R]_\infty^* = \frac{\lambda_1^2 - \lambda_2^2}{\dfrac{\lambda_1^2}{[R]_1} - \dfrac{\lambda_2^2}{[R]_2}} \qquad 9.3$$

We found: $[R]_\infty^* = 36.43$ cc., which gives $\dfrac{b_{11}+b_{22}+b_{33}}{3} = 1.445 \cdot 10^{-23}$ cc., which differs less than 1% from the predicted value.

Conclusion

The calculated values of the Kerr constants for the two conformations pertain to the Na D-line, whereas our experimental value in CCl_4, $_\infty(_mK_2) = 56 \cdot 10^{-12}$, was determined for the green mercury line. Since Kerr constants for these two wave lengths differ not more than 2% and since we have already introduced the inaccuracy of neglecting θ_1, we have disregarded the dispersion of the Kerr constant when comparing experimental and calculated values.

The experimental value can be explained by assuming that the compound is a mixture consisting of 60% of the conformation with the Cl-atom axially and 40% of the conformation with the Cl-atom equatorially.

If it is assumed that steric factors mainly determine the stability of a conformation this result is not unexpected since a Cl-atom and a methyl group have about equal size.

It will be clear that along these lines no explanation is possible for the low Kerr constant obtained from benzene solutions. In this case one might think of an explanation in terms of specific interactions e.g. of the charge-transfer type.

B. A n i s o l e

Solvent	Calc. from table	$\infty(_mK_2)$ · 10^{12}	$\mu(D)$
CCl_4	G	33.7 ± 1.4	1.25 ± 0.02
CCl_4	H	31.3 ± 1.2	1.25 ± 0.02
C_6H_6	I	13.8 ± 1.3	1.23 ± 0.03

Table Q

Other values of the dipole moment are:

1.3 D in C_6H_6 (Le Fèvre and Le Fèvre, 1950)
1.25 D in CCl_4 (Klages and Köppling, 1953)
1.28 D in C_6H_6 (Everard and Sutton, 1949)
1.27 D in CCl_4 (Aroney et al., 1960)

The value of the Kerr constant determined by Aroney et al. (1960) in CCl_4 solutions, at $25^{\circ}C$ and with the Na D-line was $\infty(_mK_2)$ = $28.8 \cdot 10^{-12}$. With anisole again we found a much lower value of the Kerr constant when determined from benzene solutions.

Conformational analysis

Aroney et al. (1960) have analyzed their data by calculating the Kerr constants for a number of conformations, differing in the position of the methoxy group with respect to the plane of the benzene ring. They find agreement with the experimental value if it is assumed that the methoxy group is rotated over an angle of 18° out of the plane of the benzene ring. We have made a similar analysis by calculating the Kerr constant for a molecule with freely rotating methoxy group and for a flat molecule, neglecting a slight exaltation of the average polarizability which was accounted for by Le Fèvre and Le Fèvre.

For both cases we use the expressions:

$$\theta_1 = \frac{1}{45kT} y; \quad y = (b_{11}-b_{22})^2 + (b_{22}-b_{33})^2 + (b_{33}-b_{11})^2 + 6b_{12}^2 +$$
$$+ 6b_{13}^2 + 6b_{23}^2 \qquad 9.4$$

$$\theta_2 = \frac{1}{45k^2T^2} z; \quad z = \mu_1^2(2b_{11}-b_{22}-b_{33}) + \mu_2^2(2b_{22}-b_{11}-b_{33}) +$$
$$+ \mu_3^2(2b_{33}-b_{11}-b_{22}) + 6b_{12}\mu_1\mu_2 + 6b_{13}\mu_1\mu_3 +$$
$$+ 6b_{23}\mu_2\mu_3 \qquad 9.5$$

which can be found in the paper of Buckingham and Pople (1955). They are especially useful when the polarizability tensor is not diagonalized. In θ_1 the difference between static and electronic polarizability is neglected.
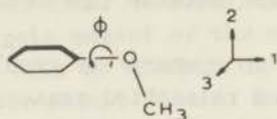
Figure 6

The C-O-C angle is taken equal to the tetrahedral angle 109°28'. The angle between the C-O-C plane and the plane of the phenyl nucleus is called ϕ. According to Klages (1954) μ_1 = -0.53 D and μ_2 = -1.13 D. Aroney et al. (1960) and Le Fèvre et al. (1963) give the following group and bond polarizabilities:

$$10^{23} b_1^{ph} = 10^{23} b_2^{ph} = 1.12 \text{ cc.}; \quad 10^{23} b_3^{ph} = 0.735 \text{ cc.}$$

$$10^{23} b_l^{C-O} = 0.089 \text{ cc.}; \quad 10^{23} b_t^{C-O} = 10^{23} b_v^{C-O} = 0.046 \text{ cc.}$$

$$10^{23} b_l^{C-H} = 0.064 \text{ cc.}$$

With these values we obtain:

$$y = (0.2965 \cos^4\phi - 0.2671 \cos^2\phi + 0.2223 \sin^2 2\phi +$$

$$+ 0.1482 \cos^2 2\phi + 0.0293 \cos 2\phi + 0.1608) \cdot 10^{-46}$$

$$z = (4.290 \cos^2\phi + 2.815 \sin^2\phi - 3.687) \cdot 10^{-59}$$

When averaging over all values of ϕ, making use of $\overline{\cos^2\phi}$ = ½, $\overline{\cos^4\phi}$ = 3/8, $\overline{\cos 2\phi}$ = 0, $\overline{\cos^2 2\phi}$ = ½, $\overline{\sin^2 2\phi}$ = ½, we find:

$$y = \quad 0.3236 \cdot 10^{-46}$$
$$z = -0.1340 \cdot 10^{-59}$$
$$_\infty(_m K_2) = \quad 2.2699 \cdot 10^{35} y + 0.552 \cdot 10^{49} z = -0.052 \cdot 10^{-12}$$

For a flat model, $\phi = 0$, we find:

$$_\infty(_m K_2) = 41.64 \cdot 10^{-12}$$

Neither the one nor the other model agrees with experiment. The measured value of $_mK$ ($32.5 \cdot 10^{-12}$) can be obtained assuming that $\phi = 19°$.

Aroney et al. mention that this model is in agreement with the supposed steric hindrance between the methyl group and ortho hydrogen atoms.

It is of some interest to compare our results with those which Klages (1954) derived from relaxation measurements. Klages tried to explain the relaxation behaviour by assuming that a fraction of the molecules has freely rotating methoxy groups, whereas the other molecules have a fixed methoxy group. In addition Klages thinks it probable that the group is jammed in the plane of the phenyl group with an ortho hydrogen atom in between two hydrogen atoms of the methyl group. Klages' conclusion is that 15% of the molecules have a jammed and 85% a freely rotating methoxy group. Our results point in the opposite direction since we would find 80% in the flat conformation and 20% freely rotating.

C. m, m' - D i a n i s y l

Solvent	Calc. from table	$_\infty(_mK_2) \cdot 10^{12}$	$\mu(D)$
CCl_4	J	187.5 ± 5.1	1.64 ± 0.03
CCl_4	K	178.1 ± 4.6	1.72 ± 0.08
C_6H_6	L	171.8 ± 9.3	1.70 ± 0.05

Table R

The averaged value for the dipole moment is 1.69 D. Klages and Köppling (1953) found 1.74 D from CCl_4 solutions. The averaged $_\infty(_mK_2)$ for CCl_4 solutions is $_\infty(_mK_2) = 183 \cdot 10^{-12}$. The determination in benzene solutions deviates less from this value than in the case of anisole. Former determinations of the Kerr constant of m,m'-dianisyl are not known.

Conformational analysis

We have calculated the Kerr constants for nine conformations of m,m'-dianisyl, see fig. 7. In the conformations a-f the planes of

the phenyl groups are parallel, in the conformations g-i they are perpendicular to each other. In conformation e the 2-axis is laid along the phenyl-O bond, in all other conformations the 1-axis is oriented along the C-C bond. In all cases the 1-2 plane is the plane of the paper. In order to simplify the calculations we have assumed that the dipole moment of the methoxy group lies in the plane of the phenyl ring to which it is attached and is oriented perpendicularly to the phenyl-O bond. With a more realistic model reflecting more precisely the results obtained with the anisole molecule the calculated values of dipole moments and Kerr constants could be somewhat different. We do not expect, however, that the changes will be important. The results are given in Table S. $_\infty(_mK_2)_D = \dfrac{2\pi N_A}{9}\,\theta_2$ is the dipole term, $_\infty(_mK_9)_A = \dfrac{2\pi N_A}{9}\,\theta_1$ is the anisotropy term. $_\infty(_mK_2) = {_\infty}(_mK_2)_A + {_\infty}(_mK_2)_D$.
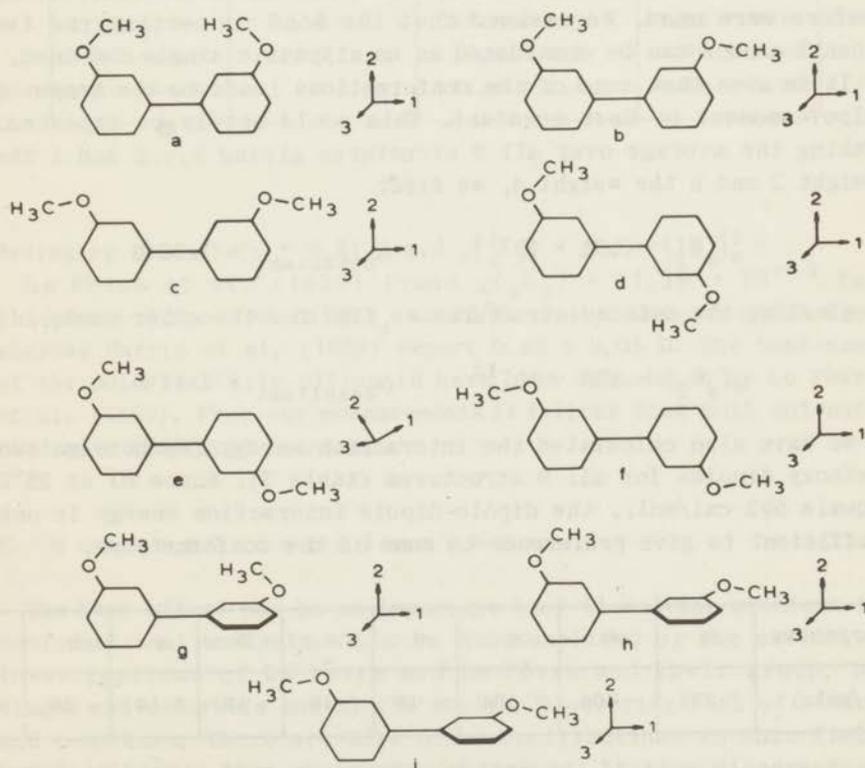
Figure 7. Conformations of m,m′-dianisyl

Conformation	a	b	c	d	e	f	g	h	i
$10^{23}b_{11}$	2.708	2.732	2.756	2.708	2.709	2.756	2.708	2.732	2.756
$10^{23}b_{22}$	2.694	2.670	2.647	2.694	2.693	2.647	2.252	2.252	2.228
$10^{23}b_{33}$	1.809	1.809	1.809	1.809	1.809	1.809	2.252	2.228	2.228
$10^{23}b_{12}$	0	-0.014	0	0.005	-0.031	-0.023	0.003	0.003	-0.011
$10^{23}b_{13}$	0	0	0	0	0	0	-0.003	0.011	0.011
$10^{23}b_{23}$	0	0	0	0	0	0	0	0	0
μ_1	0	2.15	0	0	2.48	0	0	2.15	0
μ_2	1.24	0	-1.24	0	0	0	0.62	0.62	-0.62
μ_3	0	0	0	0	0	0	-0.62	-0.62	0.62
$\mu_{Resultant}$	1.24	2.15	1.24	0	2.48	0	0.87	2.32	0.87
$\infty(_mK_2)_D \cdot 10^{12}$	74	251	62	0	310	0	-19	243	-22
$\infty(_mK_2)_A \cdot 10^{12}$	36	36	36	36	36	36	9	11	13
$\infty(_mK_2) \cdot 10^{12}$	110	287	98	36	346	36	-10	254	-9

Table S

For the calculations the same formulae and the same constants as before were used. We assumed that the bond connecting the two phenyl groups can be considered as an aliphatic single C-C bond.

It is seen that none of the conformations leads to the measured dipole moment or Kerr constant. This could hardly be expected. Taking the average over all 9 structures giving b, e, g and i the weight 2 and h the weight 4, we find:

$$\infty(_mK_2) = 158 \cdot 10^{-12} \qquad \mu_{Resultant} = 1.53 \text{ D}$$

Neglecting the twisted structures we find for the other ones:

$$\infty(_mK_2) = 193 \cdot 10^{-12} \qquad \mu_{Resultant} = 1.47 \text{ D}$$

We have also calculated the interaction energy (W) between two methoxy dipoles for all 9 structures (table T). Since RT at 25°C equals 592 cal/mol., the dipole-dipole interaction energy is not sufficient to give preference to some of the conformations.

Conformation	a	b	c	d	e	f	g	h	i
W(cal/mol.)	+ 104	- 104	+ 104	- 16	+ 16	- 16	+ 19	- 19	+ 19

Table T

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Conclusion

Although it appears to be impossible to reach a definite con-
clusion from the measurements of dipole moment and Kerr constant
as to the shape of m,m'-dianisyl one gets the impression that all
conformations are present in comparable quantities.

D. Thiophene

Thiophene has been measured in CCl_4 as well as in cyclohexane.

Solvent	Calc. from table	$_\infty(_mK_2) \cdot 10^{12}$	$\mu(D)$
CCl_4	M	11.8 ± 0.7	0.54 ± 0.01
cyclohexane	N	11.4 ± 0.6	0.51 ± 0.02
cyclohexane	O	11.4 ± 0.8	0.49 ± 0.02

Table U

Averaging leads to $\mu = 0.51$ D and $_\infty(_mK_2) = 11.5 \cdot 10^{-12}$

Le Fèvre et al. (1959) found $_\infty(_mK_2) = 11.19 \cdot 10^{-12}$ for
thiophene dissolved in CCl_4 at 25°C. For μ they found 0.54 D
whereas Harris et al. (1953) report 0.52 ± 0.05 D. The semi-axes
of the polarizability ellipsoid have been calculated by Le Fèvre
et al. (1959). From our measurements it follows that both solvents
used give identical results.

E. General conclusion

The Kerr effect may be an important tool in solving problems in
conformational analysis. This is substantiated by the extensive
investigations of Le Fèvre and Le Fèvre and their group, by
Klages and coworkers and by the earlier pioneering work of Stuart
and coworkers. There are also other contributions in this field
but they have a less systematic character. It is a disadvantage
of the method that the measurements as well as the evaluation of

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the results are rather tricky and time consuming. Consequently it has only a sense to incorporate the Kerr effect in organic investigations if it will be used regularly during a rather lengthy period. Otherwise the acquisition of the necessary experience, experimental as well as theoretical, will take relatively too much time.

REFERENCES CITED IN PART TWO

Adams, R., Kornblum, N., J. Am. Chem. Soc. <u>63</u> 192, 1941
Aroney, M., Le Fèvre, R. J. W., Shu-Sing Chang, J. Chem. Soc. <u>1960</u> p. 479
Benoit, H., Ann. Phys. (Paris) <u>6</u> 561, 1951
Bij, J. R. van der, Kooyman, E. C., Rec. Trav. Chim. <u>71</u> 837, 1952
Born, M., Ann. Physik, <u>55</u> 177, 1918
Böttcher, C. J. F., Theory of Electric Polarisation, Elsevier Publ.
Comp., Amsterdam, 1952
Briegleb, G., Z. Physik. Chem. <u>14</u> B 97, 1931
Brown, H. C., Fletcher, R. S., J. Am. Chem. Soc. <u>71</u> 1852, 1949
Buckingham, A. D., Pople, J. A., Proc. Phys. Soc. A <u>68</u> 905, 1955
Chaumont, L., Ann. Phys. (Paris) <u>4</u> 61, 1915; <u>5</u> 17, 1916
Debye, P., Sack, H., Handbuch der Radiologie, Bd. 6/2, p. 69,
Leipzig, 1934
Everard, K. B., Sutton, L. E., J. Chem. Soc. <u>1949</u> p. 2312
Gans, R., Ann. Physik <u>65</u> 97, 1921
Glancy, E. P., J. Opt. Soc. Am. <u>42</u> 357, 1952
Halverstadt, I. F., Kumler, W. D., J. Am. Chem. Soc. <u>64</u> 2988, 1942
Harris, B., Le Fèvre, R. J. W., Sullivan, E. P. A., J. Chem. Soc. <u>1953</u>
p. 1622
Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., Molecular Theory of
Gases and Liquids, Wiley, New York, 1954
Ingersoll, L. R., Phys. Rev. <u>37</u> 1184, 1931
Ingold, C. K., Structure and Mechanism in Organic Chemistry,
Cornell Univ. Press, Ithaca, N. Y. 1953, p. 136, 137
Jerrard, H. G., J. Opt. Soc. Am. <u>38</u> 35, 1948
Kerr, J., Phil. Mag. <u>50</u> 337, 446, 1875
Klages, G., Z. Naturforsch. <u>7a</u> 669, 1952
Klages, G., Köppling, E., Z. Elektrochem. <u>57</u> 369, 1953
Klages, G., Z. Naturforsch. <u>9a</u> 366, 1954
Kuhn, W., Dührkop, H., Martin, H., Z. Physik. Chem. <u>B45</u> 121, 1939
Labhart, H., Chimia (Aarau), <u>15</u> 20, 1961
Langevin, P., J. Phys. Radium <u>7</u> 249, 1910
Le Fèvre, C. G., Le Fèvre, R. J. W., J. Chem. Soc. <u>1950</u> p. 1829
Le Fèvre, C. G., Le Fèvre, R. J. W., J. Chem. Soc. <u>1953</u> p. 4041

Le Fèvre,C.G., Le Fèvre,R.J.W., Rev.Pure Appl.Chem. 5 261, 1955
Le Fèvre,C.G., Le Fèvre,R.J.W., J.Chem.Soc. 1956 p.3549
Le Fèvre,R.J.W., Purnachandra Rao,B., J.Chem.Soc. 1957 p.3644
Le Fèvre,C.G., Le Fèvre,R,J.W., Purnachandra Rao,B., Smith,M.R.,
J.Chem.Soc. 1959 p.1188
Le Fèvre,R.J.W., Sundaram,A., Pierens,R.K., J.Chem.Soc. 1960 p.479
Liptay,W., Czekalla,J., Z.Naturforsch. 15a 1072, 1960
Meyer,E.H., Otterbein,G., Physik.Z. 32 290, 1931
Mousseron,M., Granger,R., Valette,J., Bull.Soc.Chim.France 1946
p.44
Narayana Rao,D.A.A.S., Trans.Faraday Soc. 54 954,1958
O'Konski,C.T., Zimm,B.H., Science 111 113, 1950
Otterbein,G., Physik.Z. 35 249, 1934
Rudolph,H., J.Opt.Soc.Am. 45 50, 1955
Scholte,Th.G., de Vos,F.C., Rec.Trav.Chim. 72 625, 1953
Sénarmont,H.de, Ann.Chim.Phys. (2) 73 337, 1840
Siezen,G.J., Kerkhof,F., Philips Techn.Tijds. 10 157, 1948
Steppuhn,A., Z.Naturforsch. 11a 912, 1956
Stuart,H.A., Volkmann,H., Z.Physik 83 444, 1933
Stuart,H.A., Die Struktur des Freien Moleküls, Springer, Berlin,
1952
Vuks,M.F., Elfimov,V.J., Dokl.Akad.Nauk SSSR 92 29, 1953

SUMMARY

The importance that the determination of optical anisotropies may have for the study of details of molecular structure, has led to theoretical investigations of optical rotatory power of gases and liquids (part I) and to measurements of the electric birefringence of dilute solutions of organic molecules (part II).

Part I

The study of the relation between molecular quantities and measured optical activity has in the past led to a number of divergent interpretations. The origin of these discrepancies were analysed by Hoek, who at the same time found the solution to a number of the problems involved. However, his treatment did not take into account correlations in position and orientation of the molecules. In order to meet these imperfections, Goossens introduced the Onsager-Böttcher concept of the internal field into the theory. In the present thesis these correlations are accounted for by statistical mechanical methods, analogous to the methods used by Yvon and Kirkwood in their theories of dielectric polarization.

Our treatment starts from the microscopic Maxwell-Lorentz equations. The molecules are characterized by classically defined polarizability tensors, for which quantummechanical formulae are derived. The interactions between the molecules are described in terms of a Hertz vector. For a given electric field the polarizabilities determine the electrical dipole moment and two higher moments (equivalent to an electrical quadrupole and a magnetic dipole moment) of the molecule. Special attention is paid to the relation between our considerations and the A^{kl}-theory of Born as well as the one-electron model of Condon et al..

After this the averaging of the microscopic moments follows. In order to describe the interactions between the molecules adequately each molecule is considered to be at the centre of a cor-

relation sphere. The medium outside this sphere is considered, as far as the centre molecule is concerned as a continuum. The granular structure inside the sphere is reflected in effective polarizabilities.

The macroscopic moment densities are shown to satisfy a general wave equation which applies to a medium which may be anisotropic as well as optically active. With this equation the extinction theorem is proved, without introducing a particular solution of this equation, as is usually done.

Finally the theory is applied to an isotropic medium; for a simple model the influence of the reaction field is determined.

Part II

The electro-optical Kerr effect of a series of solutions was measured. The solutions consisted of 1-chloro-1-methyl-cyclohexane, anisole, m, m'-dianisyl and thiophene dissolved in carbon tetra-chloride, benzene and cyclohexane. The method was an absolute one, using a static electric field and a photo-electric detection system. Molecular Kerr constants were derived following the me-thod of Le Fèvre and Le Fèvre.

The molecular Kerr constants of anisole and thiophene, deter-mined from solutions in carbon tetrachloride appeared to be in accordance with measurements, performed almost at the same time by others. The molecular Kerr constant of 1-chloro-1-methyl-cyclohexane can be explained by assuming that the molecules are in chair conformations, 60% with the cloro atom axially, 40% with the chloro atom equatorially. The value of the molecular Kerr con-stant of m, m'-dianisyl suggests that none of the conformations occurs predominantly. The values of the molecular Kerr constants, determined from solutions of 1-chloro-1-methyl-cyclohexane and anisole in benzene, appear to be far smaller than those from solutions in carbon tetrachloride. Possibly this is due to spe-cific interactions. Special attention is paid to the influence of the birefringence of the Kerr cell windows. For some methods of measurement this influence is important, for others it is less perturbing than one would be inclined to assume.

SAMENVATTING

De belangrijke plaats die de bepaling van optische aniso-
tropieën kan innemen bij de bestudering van gedetailleerde mole-
cuulstructuren, heeft geleid tot een theoretisch onderzoek van de
optische activiteit van gassen en vloeistoffen (deel I) en tot
metingen van de electrische dubbele breking van verdunde oplos-
singen van organische moleculen (deel II).

Deel I

Het onderzoek naar het verband tussen moleculaire groot heden en
gemeten optische activiteit heeft in het verleden tot een aantal
uiteenlopende interpretaties geleid. De oorsprong van deze ver-
schillen zijn door Hoek geanalyseerd, die tevens een groot deel
van de gerezen moeilijkheden heeft opgelost. Hij heeft evenwel
geen rekening gehouden met de correlatie in plaats en oriëntatie
tussen de moleculen. Om aan dit bezwaar tegemoet te komen heeft
Goossens in de theorie gebruik gemaakt van het inwendige veld
volgens Onsager-Böttcher. In dit proefschrift worden deze corre-
laties verdisconteerd met behulp van de statistische mechanica,
naar analogie van het werk van Yvon en Kirkwood op het gebied van
de diëlectrische polarisatie.

Uitgangspunt vormen de microscopische Maxwell-Lorentz vergelij-
kingen. De moleculen worden daarbij gekarakteriseerd door klas-
siek gedefinieerde polariseerbaarheden, waarvoor naderhand
quantummechanische formules worden gegeven. De interacties tussen
de moleculen worden beschreven met behulp van een Hertzvector.
Bij een gegeven electrisch veld bepalen deze polariseerbaarheden
het electrisch dipoolmoment en twee hogere momenten (equivalent
aan een electrische quadrupool en een magnetische dipool) van het
molecuul. Er wordt gewezen op het verband tussen onze beschou-
wingen en zowel de A^{kl}-theorie van Born als het één-electron
model van Condon e.a..

Hierna volgt de middeling van de microscopische momenten. Met
het doel de interacties tussen de moleculen adequaat te beschrij-

ven wordt om het centrale molecuul een zogenaamde correlatiebol gedacht. Het medium buiten deze bol wordt ten aanzien van het centrale molecuul als een continuüm opgevat. De korrelige structuur binnen de bol wordt verdisconteerd in effectieve polariseerbaarheden.

Vervolgens wordt voor de macroscopische momentdichtheden in een medium, dat zowel anisotroop als optisch actief mag wezen, de algemene golfvergelijking afgeleid. Met behulp van deze vergelijking wordt de uitdovingsstelling bewezen, zonder gebruik te maken van een oplossing van deze vergelijking zoals gewoonlijk gebeurt.

Tenslotte wordt de theorie toegepast op een isotroop medium, waarbij voor een eenvoudig model de invloed van het reactieveld op het draaiingsvermogen wordt vastgesteld.

D e e l II

Van een reeks oplossingen van 1-chloor-1-methyl-cyclohexaan, anisool, m,m'-dianisyl en thiopheen in tetrachloorkoolstof, benzeen en cyclohexaan werd de electrische dubbele breking gemeten. Daarbij werd gebruik gemaakt van een absolute methode, een statisch electrisch veld en een foto-electrisch detectiesysteem. Voor de bepaling van moleculaire Kerrconstanten werd de methode van Le Fèvre en Le Fèvre gevolgd.

De moleculaire Kerrconstanten van anisool en thiopheen bepaald uit oplossingen in tetrachloorkoolstof bleken overeen te stemmen met metingen, vrijwel gelijktijdig verricht door anderen. De moleculaire Kerrconstanten van 1-chloor-1-methyl-cyclohexaan kan worden verklaard door aan te nemen dat de moleculen zich bevinden in stoel-conformaties, waarvan het chlooratoom in 60% axiaal en in 40% equatoriaal is geplaatst. De waarde van de moleculaire Kerrconstanten van m,m'-dianisyl wijst erop, dat geen enkele conformatie in overwegende mate voorkomt. De waarden van de moleculaire Kerrconstanten, bepaald uit oplossingen van 1-chloor-1-methyl-cyclohexaan en anisool in benzeen, bleken belangrijk kleiner te zijn dan die uit oplossingen in tetrachloorkoolstof. Mogelijk moet dit toegeschreven worden aan specifieke interacties. Aan de invloed van de dubbele breking van de vensters van de Kerrcel wordt een afzonderlijke beschouwing gewijd. Bij sommige meetmethoden is deze invloed belangrijk, bij andere minder storend dan men geneigd is te veronderstellen.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van het verloop van mijn academische studie.

Na het behalen van het einddiploma B aan de toenmalige Christelijke H.B.S. (nu Christelijk Lyceum) te Leiden in 1949, begon ik in september van dat jaar met mijn studie in de schei- en natuurkunde aan de Rijksuniversiteit te Leiden. Het candidaatsexamen (letter E) werd afgelegd in juni 1952. Mijn studie werd voortgezet onder leiding van de hoogleraren Dr.L.J. Oosterhoff, Dr.S.R. de Groot en Dr.C.J.F. Böttcher. Het doctoraalexamen met hoofdvak theoretische organische chemie en bijvakken theoretische natuurkunde en fysische chemie werd afgelegd in october 1955.

Van april 1953 tot november 1958 was ik verbonden als assistent aan de afdeling voor Theoretische Organische Chemie. Het onderzoek op het gebied van het Kerreffect, zowel experimenteel als theoretisch, waarmee ik onder leiding van Prof.Dr.L.J. Oosterhoff reeds voor mijn doctoraalexamen was begonnen, vond in deze periode plaats. In november 1954 werd mij door de Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek de gelegenheid geboden tot een verblijf van 2 maanden aan de Heald Green Laboratories van de British Rayon Research Association te Manchester, Engeland, om onder leiding van Dr.G. Porter (thans hoogleraar te Sheffield) ervaring te verkrijgen met zijn apparatuur voor flitsfotolyse.

Van november 1958 tot november 1960 moest ik mijn studie onderbreken voor de vervulling van de militaire dienstplicht. Hierna volgde mijn aanstelling als wetenschappelijk ambtenaar 1e klasse aan de afdeling voor Theoretische Organische Chemie te Leiden, en werd ik in staat gesteld tot het theoretisch onderzoek op het gebied van de optische rotatie.

De resultaten van deze onderzoekingen en van het experimentele werk aan het Kerreffect zijn grotendeels in dit proefschrift beschreven.
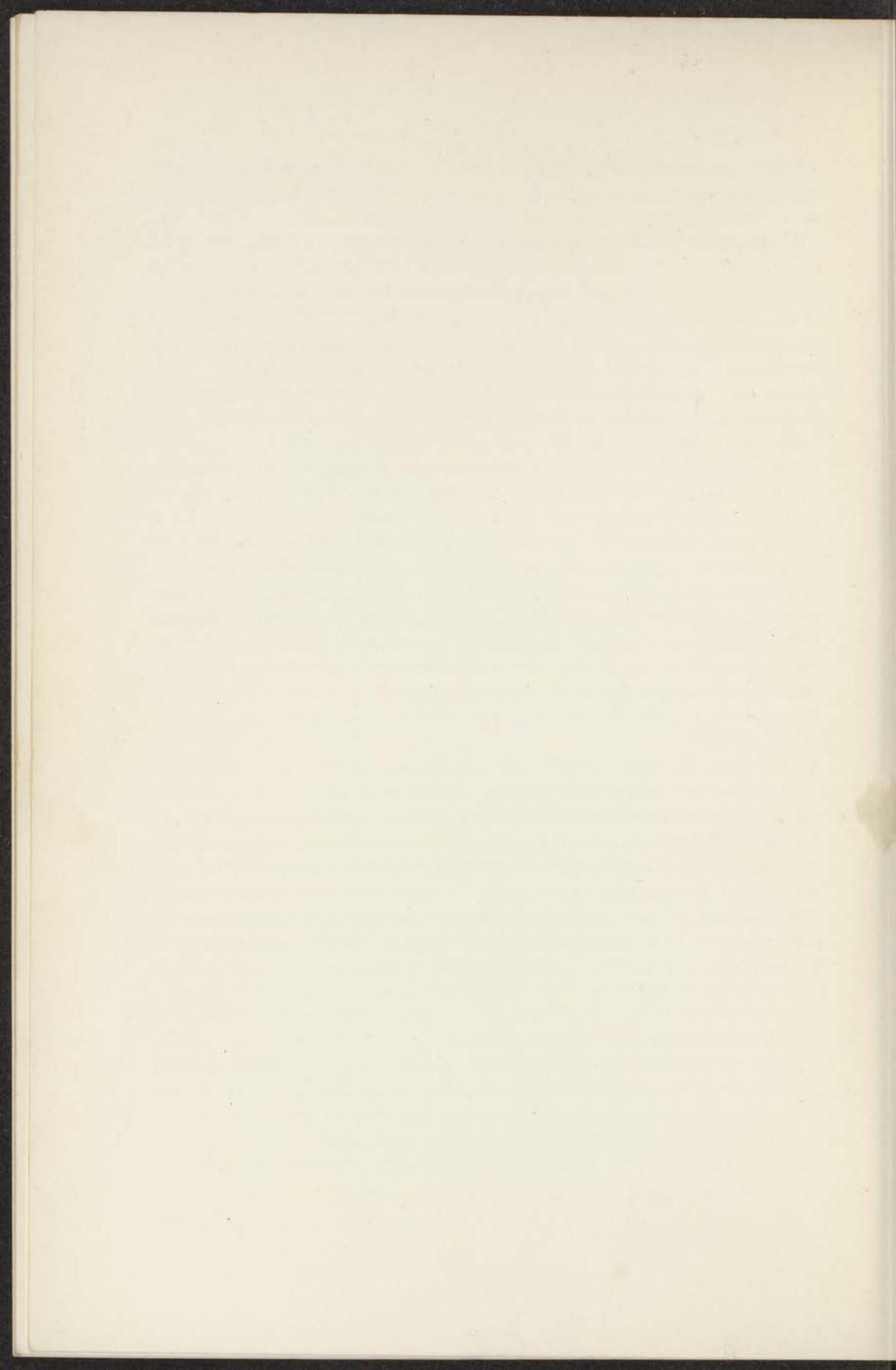
STELLINGEN

1. Een cel, waarvan de dwarsdoorsnede van de binnenkant der elec-
troden de vorm heeft van twee elkaar toegevoegde orthogonale
hyperbolen, kan voordelen bieden boven de door Buckingham en
Disch gebruikte meetcel voor de bepaling van het quadrupool-
moment van CO_2.

> A.D.Buckingham en R.L.Disch, Proc.Roy.Soc.
> (London) A <u>273</u> 275, 1963.

2. Hoewel moleculen die bepaalde symmetrie-elementen hebben, zoals
een vlak van symmetrie, gewoonlijk niet tot de optisch actieve
verbindingen gerekend worden, is het zeer goed mogelijk dat
deze moleculen in een anisotroop milieu wel verschijnselen van
optische activiteit vertonen.

3. De uitspraak van Margenau en Murphy: "...that the solution of
a differential equation is not an altogether mechanical matter
and that caution must be used at every step" wordt door het
door hen gegeven voorbeeld niet doeltreffend geïllustreerd.

> H.Margenau en G.M.Murphy, The Mathematics of
> Physics and Chemistry, p.63, Van Nostrand,
> New York, 2nd ed., 1959.

4. De door Streitwieser en Nair toegepaste iteratiemethode in hun
ω-techniek voor geconjugeerde systemen kan door een beschouwing
van de pseudo-fout belangrijk worden bekort.

> A.Streitwieser en P.M.Nair, Tetrahedron <u>5</u> 149,
> 1959.

5. De bepaling van absolute brekingsindexveranderingen onder in-
vloed van een homogeen uitwendig electrisch veld kan een waar-
devolle bron van informatie over hyperpolariseerbaarheden
geven.

> H.A.Stuart, Hand- und Jahrbuch der Chemischen
> Physik <u>10</u>/III p.57, Leipzig 1939.

6. De wijze waarop Buckingham c.s. de optische hyperpolariseer-
   baarheden beschrijven is onjuist.

A.D.Buckingham en J.A.Pople, Proc.Phys.Soc.
A 68 905, 1955.
A.D.Buckingham en M.J.Stephen, Trans.Faraday
Soc. 53 884, 1957.

7. Het model dat Kunkel en Tiselius gebruiken voor de interpretatie
   van meetresultaten bij papierelectroforese wordt door McDonald
   met een onjuiste argumentering aangevallen.

H.J.McDonald, Ionography, p.60,79, Year Book
Publ., Chicago, 1955.
H.G.Kunkel en A.Tiselius, J.Gen.Physiol. 35
89, 1952.

8. De verklaring die Stillo geeft voor de isomerisatie van precal-
   ciferol naar calciferol is aanvechtbaar.

H.S.Stillo, Thesis, Michigan State University,
p.141, 1959.

9. De ladingen die Pauling toekent aan de atomen in het sulvaniet-
   rooster zijn onwaarschijnlijk.

L.Pauling, The Nature of the Chemical Bond,
p.445, Cornell Univ.Pr.1960.

10. Het waardevast maken van elk inkomen genoten uit arbeid of
    vroeger verrichte arbeid, zal kunnen leiden tot een verzwakking
    van de rem, die thans nog bestaat op een voortschrijdende loon-
    en prijsinflatie.