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The Optical Properties of Nonpolar Liquids

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A theory of the refraction, Kerr effect and light scattering for liquids with nonpolar axially symmetric molecules is developed. The molecules are assumed to possess a limited freedom of rotation. This assumption alone does not alter the classical equations. It is necessary to consider the quasi-crystalline grouping of neighboring molecules which produces an anisotropic polarization field. The anisotropy of the Lorentz forces is calculated by combining the classical cavity method with Ewald's lattice theory. It is shown that the procedure of Raman and Krishnan is not justified. With a low potential barrier the quasi-crystalline grouping gives an increase of the refraction, Kerr effect, depolarization and intensity of the Rayleigh scattered light. This is true also for an arbitrarily high potential barrier, provided the anisotropy of the Lorentz force is sufficiently large. These results agree with the observed increase of the refraction in compressed gases and in some solids, and with the observed increase of the depolarization in compressed gases and in liquids near the critical temperature. The observations in liquids are explained by considering a moderate anisotropy of the Lorentz force and a potential barrier of finite height. In this case the molar refraction is slightly smaller than that of the ideal gas. No large deviations from the Lorentz-Lorenz equation can be expected even if the anisotropy is considerable. The refraction changes with pressure and temperature and its dispersion differs from that of the gas. The depolarization and the intensity of the scattered light are considerably smaller than, and the Kerr constant is only a fraction of, the values derived from the classical equation. The classical relations between depolarization and intensity and between Kerr constant and depolarization are only approximate. The theory is applied to benzene. It is assumed that the molecules have the same polarizabilities in the liquid and gaseous state. All observations can be explained by assuming a potential barrier of about 8.8 kT and an anisotropy of the Lorentz force which is in good accordance with the results of the x-ray analysis of the liquid structure.

IT is a well-established fact that the classical theories of refraction, light scattering and the electro-optical Kerr effect fail when applied to liquids. In liquids the molecules appear to have a slightly decreased polarizability and a much smaller optical anisotropy than in the gas. Since for most substances the absorption-spectrum is essentially the same in the gaseous, liquid and solid phase, these changes cannot be due to a change of the molecular structure. They must be connected with the fact that in liquids the molecules cannot rotate and translate as freely as in a gas. In a qualitative way the apparent decrease of the optical anisotropy can be understood by considering the anisotropic Lorentz force. Raman and Krishnan[1] have given a theory of this effect, but Stuart and Volkmann[2] have criticized their assumptions and we shall point out the inadequacies of their arguments.

Recent work has shown that in a liquid the positions and orientations of the molecules are not random. The structure of a liquid can be described by considering an arbitrarily chosen molecule. Due to the dense packing and the intramolecular forces the nearest neighboring molecules tend to assume definite preferred positions with respect to the molecule considered. They form a quasi-crystalline or cybotactic group. For anisotropic molecules these groups are anisotropic. Hence the neighboring molecules exert forces on the central molecule which prevent its free rotation. Quasi-crystalline grouping and hindered rotation are closely interrelated, but the calculation is simplified by considering their effects separately.

THE INFLUENCE OF HINDERED ROTATION

We consider a molecule with axial symmetry. b_1, $b_2=b_3$ are its polarizabilities. If the molecule is polar its permanent moment μ is parallel to the axis of symmetry. Following the method of Debye[3] we can assume that the axis of each molecule has at every instant a definite preferred direction. The energy $V(\Theta)$ is required to deflect the axis by an angle Θ from its preferred position. For nonpolar symmetric molecules, e.g., CO_2, C_6H_6, the potential hill is symmetric with respect to two minima at $\Theta=0$ and $\Theta=\pi$. For more

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[1] C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. **A117**, 589 (1928); Phil. Mag. **5**, 498 (1928).

[2] H. A. Stuart and H. Volkmann, Zeits. f. Physik **83**, 461 (1933).

[3] P. Debye, Physik. Zeits. **36**, 100, 193 (1935).

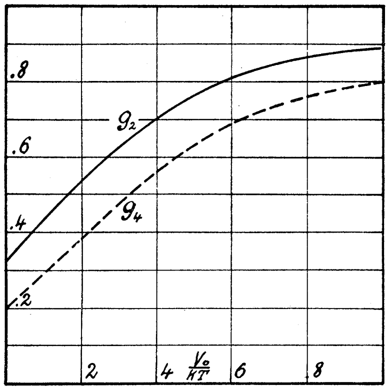

FIG. 1. The functions $g_2(V_0/kT)$ and $g_4(V_0/kT)$ for a symmetric potential barrier $V=V_0(1-\cos^2\theta)$.

complex molecules and probably for most polar molecules $\Theta=0$ gives the only minimum. Using classical statistics one finds the average polarizabilities β of the molecule. If the field is acting parallel to the preferred direction

$$\beta_1=b_2+(b_1-b_2)g_2+(g_2-g_1^2)\mu^2/kT \qquad (1)$$

and for a field normal to the preferred direction

$$\beta_2=\beta_3=\tfrac{1}{2}[(b_1+b_2)-(b_1-b_2)g_2 + (1-g_2)\mu^2/kT]. \qquad (1')$$

Here we have introduced a set of functions

$$g_n(V/kT)=\frac{\int_0^\pi \exp(-V/kT)\cos^n\Theta\sin\Theta d\Theta}{\int_0^\pi \exp(-V/kT)\sin\Theta d\Theta}. \qquad (2)$$

If $V=V_0(1-\cos\Theta)$, g_n can be expressed in terms of Langevin's function $L(x)=\operatorname{cotgh} x-1/x$, $g_1=L(V_0/kT)$, $g_2=1-2L(V_0/kT)kT/V_0$. For a symmetric potential hill $g_{2n+1}=0$. The simplest example of a symmetric potential barrier is $V=V_0(1-\cos^2\Theta)$ which gives

$$g_2=\left(\tfrac{1}{2}x^{-\frac{1}{2}}\exp x\Big/\int_0^{x^{\frac{1}{2}}}\exp t^2dt\right)-\tfrac{1}{2}x^{-1},$$

$$x=V_0/kT, \quad \text{and} \quad g_4=g_2-(3g_2-1)/2x.$$

The latter two functions are plotted in Fig. 1. g_2 has the limiting values $\frac{1}{3}$ for free rotation and 1 for no rotation. g_4 varies between 0.2 and 1.

In the classical theory it is assumed that the field acting on any molecule is parallel to the applied field E and has the value $E+4\pi I/3$, where I is the polarization. Since all angles between the field and the preferred directions occur with equal probability the average molar polarization P can be calculated in the usual way, giving

$$P=(\epsilon-1)M/(\epsilon+2)\rho=(4\pi/3)A\tfrac{1}{3}(\beta_1+2\beta_2)$$
$$=(4\pi/9)A[(b_1+2b_2)+(1-g_1^2)\mu^2/kT].$$

Hence with the classical assumption the molar refraction $R=(4\pi/9)A(b_1+2b_2)$ will not be changed whatever the form of the potential barrier may be. Furthermore, if the potential hill is symmetric, the dipole-contribution also will not be altered. Hindered rotation reduces the dipole term only if $V(\Theta)$ is asymmetric. We shall show below that analogous conclusions hold also for the Kerr constant and the scattering of light.

Experiments, however, show that neither polar nor nonpolar liquids satisfy the Lorentz-Lorenz equation. According to Stuart and Volkmann[2] the differences between the theoretical and the measured values of the Kerr constant and the depolarization are equally large for either type of molecule. Hence Debye's theory of hindered rotation, while it may explain the dielectric constant and the Kerr effect of some special polar liquids, is not sufficient to account for the optical properties of most liquids.

Our further considerations are confined to nonpolar liquids. For these the classical assumption $F=E+4\pi I/3$ leads always to the Lorentz-Lorenz equation. Hence it is necessary to abandon this assumption and replace the isotropic by an anisotropic Lorentz force.

THE ANISOTROPIC LORENTZ FORCE IN CRYSTALS

Inasmuch as the structure of a liquid has a closer resemblance to that of a crystal than to that of a gas, it is natural to approach the problem of the inner field by considering first an ideal crystal. The theory of the Lorentz force in a lattice was developed by Ewald[4] and generalized by Born.[5] The writer[6] has given a simplified derivation.

We consider an infinite lattice whose elementary cell contains only one atom situated at the

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[4] P. P. Ewald, Ann. d. Physik **49**, 1, 117 (1916).

[5] M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, Vol. 24, p. 770.

[6] H. Mueller, Phys. Rev. **47**, 948 (1935).

origin of the cell. If x, y, z are the axes of the optical index ellipsoid, the Lorentz force acting on any atom can be written

$$F_x=E_x+4\pi L_x I_x. \tag{3}$$

The "Lorentz factors" L_x, L_y, L_z can be derived from Ewald's lattice potential[7]

$$\bar{\psi}=\psi-1/r, \qquad L_x=\Delta/4\pi(\partial^2\bar{\psi}/\partial x^2)_0.$$

Poisson's equation requires

$$L_x+L_y+L_z=1. \tag{4}$$

The Lorentz factors depend on the shape, but not on the size of the elementary cell. Previously the author[6] has given the values of $L_x=L_y$ and L_z for tetragonal lattices. Fig. 2 gives these factors for simple hexagonal lattices. They depend on the ratio c/a, where c is the lattice spacing in the direction of the hexagonal axis, and a is the distance to the nearest neighbors normal to the axis. The results are very similar to those for tetragonal lattices.

We observe again that if c/a is moderately large $L_x=kc/a$ and $L_z=1-2kc/a$. Since with $c/a>1$ we have a layer lattice, this result has the following simple interpretation: In a layer lattice the Lorentz force can be calculated by considering the atoms continuously distributed in all layers except the layer in which the atom is situated. For a field E_z the continuous distribution gives the field $4\pi I_z$ and hence contributes 1 to the factor L_z. The dipoles in the same layer give a negative field which can readily be calculated by direct summation. Thus one finds $k=0.359$ for tetragonal and $k=0.370$ for hexagonal lattices. These factors agree with the slope[8] of the L_x-curves if $c/a>1.5$.

Similarly for small values of c/a one has $L_z=k'(a/c)^2$, which means that in a chain lattice it is necessary to consider the discontinuous structure along only a single chain of atoms. k' is therefore given by a simple infinite sum and has the values 0.3826 and 0.3313 for tetragonal and hexagonal lattices respectively. This is a good approximation if $c/a<0.6$. If c/a differs little from unity one can use a similar approximation by calculating the field of the dipoles within a rectangular box. The validity of the latter method was demonstrated in a previous paper.[6]

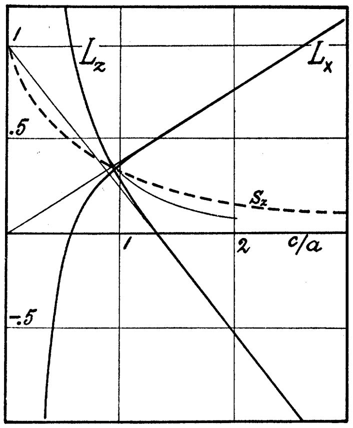

FIG. 2. The Lorentz factors for simple hexagonal lattices and the approximations for small and large values of c/a. Dotted curve: Raman and Krishnan's approximation.

In evaluating the field of the dipoles in a single layer or chain one again can consider the atoms at a large distance as continuously distributed. Hence the Lorentz factors are determined if we know the distribution of the few nearest neighbors only. Even in a crystal the atoms more than a few atomic distances away can be looked upon as forming a continuum.

This result justifies the well-known cavity method for calculating the inner field[9] and furnishes the basic principle for evaluating the Lorentz force in liquids.

Fig. 2 illustrates another important point. Following a suggestion of Havelock,[10] Raman and Krishnan[1] assume that for an anisotropic structure an ellipsoidal cavity can be found which has the property that the atoms within give no contribution to the Lorentz force. This assumption is incorrect because L can take negative values, whereas the cavity method leads always to positive values. Without justifying themselves Raman and Krishnan postulate furthermore that the hypothetical ellipsoid has an axial ratio c/a. Hence they assume a Lorentz factor

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[7] The lattice potential ψ is the electrostatic potential of a charge distribution consisting of discrete unit positive charges at the lattice points and a uniform constant negative charge density $-1/\Delta$, where Δ is the volume of the elementary cell. If the charge at the origin is missing the potential is $\bar{\psi}=\psi-1/r$ and the derivative must be taken for the values $x=y=z=0$.

[8] In the paper mentioned (reference 6) we estimated from the graph for tetragonal lattices $2k=0.72$. The direct summation gives 0.718.

[9] This result shows also that in general it is advisable to use an anisotropic cavity for an anisotropic crystal.

[10] T. H. Havelock, Proc. Roy. Soc. **A80**, 31 (1908).

$$s=s_z=\frac{1-\epsilon^2}{\epsilon^2}\left(\tfrac{1}{2}\epsilon\ln\frac{1+\epsilon}{1-\epsilon}-1\right), \qquad (5)$$

where ϵ is the eccentricity $\epsilon^2=1-(a/c)^2$. If $a>c$ one takes $\epsilon^2=(a/c)^2-1$ and obtains

$$s_z=\frac{1+\epsilon^2}{\epsilon^2}\left(1-(1/\epsilon)\tan^{-1}\epsilon\right). \qquad (5')$$

s_x and s_y are determined by the relations $s_x=s_y$ and $s_x+s_y+s_z=1$. In Fig. 2 the dotted curve gives the values of s_z. Raman and Krishnan's assumption $s_z=L_z$ is obviously untenable.

The use of the s factors is however justified if the cavity method is correctly applied. The cavity can have any size as long as it includes at least the nearest 20 or 30 neighboring atoms. We find then $F_x=E_x+4\pi s_x I_x+F_x'$. Comparison with (3) gives

$$F_x'=4\pi(L_x-s_x)I_x=4\pi\gamma_x I_x, \qquad (6)$$

where $\gamma_x+\gamma_y+\gamma_z=0$, hence $\gamma=\gamma_z=-2\gamma_x=-2\gamma_y=L_z-s_z$.

F' is the field of the finite number of dipoles within an ellipsoidal cavity, the axes of which are parallel to the optical axes of the crystal. The field F' does not depend on the size of the ellipsoid, but only on its eccentricity. Consequently the field of the dipoles within a uniformly polarized shell, bordered by two concentric ellipsoids of equal eccentricities is zero at the center.

The above results hold also for molecular lattices. In a forthcoming paper it will be shown that they are also valid for "diffuse" lattices in which the atoms or molecules oscillate about their equilibrium positions.

The Lorentz Force in Liquids

From the work of Stewart,[11] Warren,[12] Bernal and Fowler,[13] Debye,[3] Frenkel[14] and others, the following assumptions concerning the structure of liquids seem reasonable. For rod- or disk-shaped molecules the preferred positions of the nearest neighboring molecules are arranged in a lattice with axial symmetry. In many liquids the x-ray analysis[12] points to a simple hexagonal lattice.[15] The preferred orientation of the molecule considered and of its nearest neighbors will have the direction of the symmetry axis of the lattice. The position and orientation of any distant molecule is arbitrary.

The environment of a molecule can be divided into three regions:

1. *The cybotactic region*, with a pronounced lattice structure. Within it all molecules have the same preferred orientation. The dimensions of this zone must be much smaller than the wavelength of light. We assume that it includes at least 20 to 30 molecules and that it has the shape of an ellipsoid of rotation whose eccentricity ϵ is smaller than the eccentricity of the ellipsoid representing the shape of the molecule.

2. *The continuous region.* This includes all distant molecules whose positions and orientations are independent of those of the molecule upon which we fix our attention. As far as this molecule is concerned the distant molecules act as if forming a continuous distribution of matter. This region, extending to infinity, starts at a certain boundary, which is assumed to be an ellipsoid, larger but of the same eccentricity as the one limiting the cybotactic zone.

3. *The intermediate region between 1 and 2.* Here the molecules are only slightly influenced by the intramolecular forces exerted by the central molecule. This region may be divided into a series of concentric ellipsoidal shells of constant eccentricity ϵ. Every molecule within one shell will be influenced in the same manner by the central molecule.

The molecule upon which we fix our attention may be any arbitrary molecule. The symmetry axis of its cybotactic lattice can take on any direction with equal probability. We assume that no outer influence, not even that of a strong electric field, can change the distribution of the preferred directions to any marked degree.[16] The preferred orientation of a molecule changes slowly with time, but this change is assumed to

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[11] G. W. Stewart, Trans. Faraday Soc. **29**, 982 (1933).

[12] B. E. Warren, Phys. Rev. **44**, 969 (1933).

[13] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[14] J. Frenkel, Acta phys. chem. **3**, 663 (1936).

[15] This is the simplest possible assumption, but it is not essential for our calculation.

[16] Investigations of the light scattering and the x-ray diffraction of liquids in a strong electric field have furnished no evidence to the contrary.

be negligible during the period of a light wave.[17]

Under the influence of an electric field E the liquid acquires an average polarization I in the direction of E. Within a cybotactic group, however, the polarization is not in the direction of the field. Hence we introduce the concept of the "local polarization J." J varies continuously throughout the liquid. It depends on the local preferred direction.

The results of the preceding section give for the Lorentz force in a liquid

$$F_x=E_x+4\pi s_xI_x+4\pi\gamma_xJ_x. \tag{7}$$

$4\pi s_xI_x$ is the field of the distant molecules which act as if they were a continuum. $4\pi\gamma_xJ_x$ is according to Eq. (6) the field of the dipoles in the cybotactic group. The dipoles in the intermediate range give no field, because, as we have seen, the field of a uniformly polarized ellipsoidal shell is zero at the center. The three equations (7) give the components of F parallel and normal to the preferred axis. Hence

$$J_x=N\beta_2F_x;\quad J_y=N\beta_2F_y;\quad J_z=N\beta_1F_z, \tag{8}$$

where β_1 and β_2 are the average polarizabilities of the molecule defined by Eq. (1). $N=\rho A/M$ is the number of molecules per cc, ρ, the density, A, Avogadro's number and M the molecular weight. Introducing Eq. (8) in Eq. (7) gives

$$F_x=l_x(E+4/3\pi I)_x, \tag{9}$$

where, since $I=(n^2-1)E/4\pi$,

$$\begin{aligned} l_x=l_y&=[1-3/2(s-\tfrac{1}{3})(n^2-1)/(n^2+2)]/(1+2\pi\gamma N\beta_2),\\ l_z&=[1+3(s-\tfrac{1}{3})(n^2-1)/(n^2+2)]/(1-4\pi\gamma N\beta_1). \end{aligned} \tag{10}$$

By combining Eqs. (9) and (7) one gets three equations for J_x, J_y and J_z. Finally, since I is obviously the average value of the local polarization J, $I=\bar{J}$, one can eliminate J and calculate the molar refraction R_L of the liquid.

$$R_L=(n^2-1)M/(n^2+2)\rho=\frac{4}{3}\pi A\frac{\frac{1}{3}[\beta_1/(1-4\pi\gamma\beta_1N)+2\beta_2/(1+2\pi\gamma\beta_2N)]}{1-(4/3)\pi N(s-\frac{1}{3})[\beta_1/(1-4\pi\gamma\beta_1N)-\beta_2/(1+2\pi\gamma\beta_2N)]}. \tag{11}$$

This expression can be simplified. The denominator corresponds to the correction given by Raman and Krishnan.[18] But since the boundary of a cybotactic group has a smaller eccentricity than the molecule, our value of $(s-\frac{1}{3})$ is much smaller than theirs. In fact this correction is so small that it can be neglected in most cases. Therefore we take $s=\frac{1}{3}$, which means that the cybotactic groups are approximately spherical. Even if they have elliposidal shape, the assumption $s=\frac{1}{3}$ does not alter the results by more than a fraction of one percent, because a change of s alters the value of $\gamma=L_z-s$ in such a way, that l_x, l_z and R_L remain almost unchanged.

If we introduce

$$\begin{aligned} &p=b_1/b_2,\quad b=\tfrac{1}{3}(b_1+2b_2),\\ &B=[1-g_2(1-p)]/(p+2),\\ &x=12\pi Nb(L_z-\tfrac{1}{3})=9(L_z-\tfrac{1}{3})\rho R_0/M,\\ &R_0=4/3\pi Ab. \end{aligned} \tag{12}$$

Eq. (11) takes the simple form

$$R_L/R_0=B/(1-xB)+(1-B)/(1+\tfrac{1}{4}x(1-B)). \tag{13}$$

R_0 is the molar refraction of the gas, x depends on the anisotropy of the quasi-crystalline structure and B on the freedom of rotation. Since b_1, b_2 and R_0 can be obtained from measurements in the gaseous state, Eq. (13) contains only two unknown parameters L_z and g_2. They are characteristic of each liquid. g_2 varies with the temperature and the density. We do not expect a temperature dependence of L_z, except near the critical temperature of the liquid.

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[17] The characteristic frequencies of mutual vibration of the molecules are in the far infrared. C. H. Cartwright, Phys. Rev. **49**, 470 (1936).

[18] Raman and Krishnan's relation is obtained if we put $s=L_z$, hence $\gamma=0$ and $\beta_1=b_1$, $\beta_2=b_2$. The latter relations imply that the molecules have entirely lost their freedom of rotation ($g_2=1$) Raman and Krishnan's equation gives results of the correct order of magnitude because it contains two errors which partly compensate each other. The anisotropy of their Lorentz field is too small ($s<L_z$, see Fig. 1), whereas the effect of hindered rotation is taken too large.

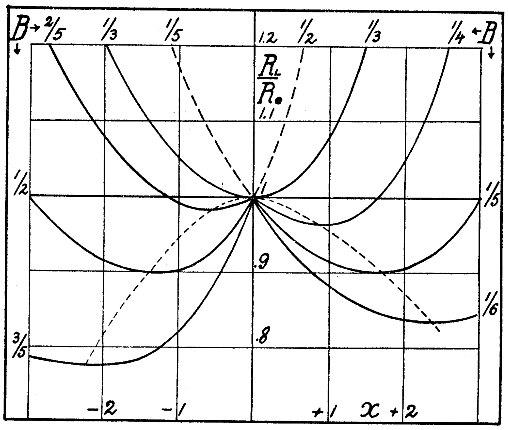

FIG. 3. The molar refraction of liquids. The variable $x=9(L_z-1/3)\rho R_0/M$ depends on the anisotropy of the Lorentz force, the parameter B on the potential barrier and the optical anisotropy of the molecule. The dotted curve gives the minima of the curves.

THE MOLAR REFRACTION OF LIQUIDS. BENZENE

The classical work of L. Lorenz led to the conclusion that the molar refraction is the same in the liquid and gaseous state. This fact has frequently been mentioned as an argument against anisotropic Lorentz forces. But more accurate measurements have shown that the refraction of a liquid is usually slightly smaller than that of its vapor, and that it varies with temperature and pressure. In addition the dispersion of R_L is larger than the dispersion of R_0.

Although these differences are relatively small, they are nevertheless too large to be explained by changes of the polarizabilities of the molecule.[19] Our theory accounts for all these changes without postulating any alteration in the polarizabilities.

In Fig. 3 R_L/R_0 is plotted as a function of x for various values of B. Since x is of the order of magnitude of $9(L-\frac{1}{3})(n^2-1)/(n^2+2)$ its absolute value is probably never larger than 3. From Fig. 2 it follows that x is positive for disk-shaped and negative for rod-shaped molecules. The parameter B varies between $\frac{1}{3}$ for $g_2=\frac{1}{3}$, and $p/(p+2)$ for $g_2=1$. Since for most molecules $\frac{1}{3}<p<3$ it is sufficient to vary B between the limits 0.15 and 0.6. Rod-shaped molecules usually have $p>1$ and hence $B>\frac{1}{3}$, while for disk-shaped molecules $B<\frac{1}{3}$.[20]

The curves in Fig. 3 have a minimum $9B(1-B)/(3B+1)$ for $x=2(1-3B)/3B(1-B)$ and R_L/R_0 is 1 for $x=0$ and for $x=(B+1)(1-3B)/B(1-B)$. If the molecules can rotate freely or almost freely the anisotropy of the Lorentz force demands $R_L>R_0$. It is probable that this condition exists in compressed gases, which would explain the increase of the molar polarization of CO_2 with pressure.[19] If the anisotropy is very large we always get $R_L>R_0$, even if no rotation exists. The Lorentz force reaches its largest anisotropy in the crystalline state. Hence it is not surprising that the molar polarization of solid benzene is larger than that of its vapor.[19]

The case $R_L<R_0$ occurs only if we have hindered rotation together with a moderate anisotropy of the Lorentz force. These are exactly the conditions existing in liquids. We notice that in all cases of practical importance $R_L/R_0>0.9$. Hence the approximate validity of the Lorentz-Lorenz equation cannot be advanced as an argument against anisotropic Lorentz forces.

Since we have no direct information concerning the values of g_2 and L_z we are not able to predict the refraction of a liquid. Inversely, however, we can find approximate values of these parameters from the observed values of R_L.

We will discuss the procedure for benzene. According to Stuart[21] the polarizabilities are $b_1=63.5\ 10^{-25}$, $b_2=b_3=123.1\ 10^{-25}$ hence $p=0.516$. In Fig. 4 R_L/R_0 is given as a function of x for various values of g_2. Wasastjerna[22] has determined $R_0=27.20$ (D-line) and $R_L=26.18$ (room temperature), hence $R_L/R_0=0.962$. Fig. 4 shows that this value can be understood only if g_2 is larger than 0.775. If we assume a potential $V_0(1-\cos^2\theta)$ this indicates, according to Fig. 1,

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[19] The work of Fajans and Joos (Zeits. f. Physik **23**, 1 (1924)) and the theory of photoelasticity (H. Mueller, Phys. Rev. **47**, 947 (1935)) show that such changes must occur in solids, but in liquids they cannot play an important part as shown by the fact that the molar polarization of CO_2 increases with pressure (F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36**, 754 (1930)) and that the polarization of solid benzene is larger than that of benzene vapor (C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1932)).

[20] This is not true in some exceptional cases, e.g., formic acid and acetic acid. For these substances our theory predicts $R_L>R_0$.

[21] H. A. Stuart, *Molekülstruktur* (Berlin 1934), p. 173. These polarizabilities are determined from the Kerr effect of the vapor. Cabannes' measurement of the depolarization of the scattered light gives $p=0.505$.

[22] J. A. Wasastjerna, Soc. Sc. Fennica, Comm. Math. Phys. **2**, No. 13 (1924). The corresponding values of the molar polarization are $P_L=26.61$ $P_0=27.01$, hence $P_L/P_0=0.985$. The ratio p_0 of the static polarizabilities is probably larger than p. $P_{\text{solid}}=28.5$.

that the potential barrier must be higher than 5.2 kT.

A value for x and a closer estimate of g_2 can be obtained if we consider the dispersion. A change of wave-length does not affect g_2 and L_z, since they depend only on the liquid structure, but it does change the value of R_0 and hence of x. The slope of the curves R_L/R_0 for $g_2=$const. is related to the difference between the dispersions of R_L and R_0. According to Wasastjerna[22] $R_F-R_C=0.74$ for liquid benzene, and $R_F-R_C=0.68$ for the vapor. From these data one estimates $d(R_L/R_0)/dx=0.12/x$. Lines corresponding to these slopes are shown in Fig. 4. We see that there is only one solution for which $R_L/R_0=0.962$ and for which the slope suits the observed difference of dispersions, namely $x=1.8$ and $g_2=0.875$. This corresponds to a potential hill of about 8.8 kT, a value of the same order of magnitude as those given by Debye[3] and Andrade.[23]

With $\rho=0.881$, $R_0=27.2$, $M=78.05$, we calculate from $x=9(L_z-\frac{1}{3})\rho R_0/M$ (Eq. 12) $L_z=0.98$. If we assume a simple hexagonal structure of the cybotactic group we find from Fig. 2 that this corresponds to $c/a=0.56$. According to the considerations of de Boer[24] a hexagonal structure seems a good approximation. He reports that recent x-ray work gives $c=3.5$ to 3.6A. To account for the observed density we must have $M/A\rho=ca^2 3^{\frac{1}{2}}/2$ or $c/a=0.50$ to 0.53, which is a surprisingly good verification of our result.

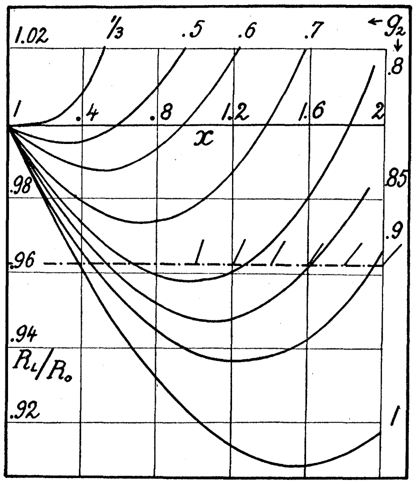

FIG. 4. The molar refraction of benzene. The dotted line gives the observed value. The short lines indicate the slopes $d(R_L/R_0)/dx$ required by the observed dispersions.

In view of the fact that the value of p is accurate to only about 3 percent and that a small part of the change of dispersion may be due to the shift of the absorption lines,[25] the above results are somewhat inaccurate. The true solution probably lies within the ranges $1.4<x<1.8$ and $0.82<g_2<0.9$.

With this solution we can now estimate the order of magnitude of the temperature–and the pressure variation of R_L. If we assume $L_z=$const. and abbreviate $R_L/R_0=r$, $\varphi=V_0(\rho)/kT$ we have

$$1/R_0\frac{\partial R_L}{dT}=\frac{1}{\rho}\frac{d\rho}{dT}\left[x\frac{\partial r}{\partial x}+\frac{\partial r}{\partial g_2}\frac{dg_2}{d\varphi}\varphi\frac{dV_0}{d\rho}\frac{\rho}{V_0}\right]-\frac{\partial r}{\partial g_2}\cdot\frac{dg_2}{d\varphi}\frac{\varphi}{T}, \tag{14}$$

$$1/R_0\frac{\partial R_L}{\partial p}=\frac{1}{\rho}\frac{d\rho}{dp}\left[x\frac{\partial r}{\partial x}+\frac{\partial r}{\partial g_2}\frac{dg_2}{d\varphi}\varphi\frac{dV_0}{d\rho}\frac{\rho}{V_0}\right]. \tag{15}$$

With the values $(1/\rho)(d\rho/dT)=-1.21\ 10^{-3}$, $(1/\rho)(d\rho/dp)=9.5\ 10^{-11}$, $x\partial r/\partial x=0.12$, $\partial r/\partial g_2=-0.44$ (the latter value estimated from Fig. 4) $dg_2/d\varphi=0.018$ (from Fig. 1), $\varphi=8.8$, $T=290$ we get roughly $(1/R_0)\partial R_L/\partial T=2$ to 3 10^{-4}. The experimental value is 1.22 10^{-4}. The theoretical value of $(1/R_0)\partial R_L/\partial p$ depends largely on $V_0(\rho)$. If we assume[23] $V_0=c\rho^t$ close agreement with the observed value $-0.98\ 10^{-11}$ is obtained for $t=3$. But this result depends very much on the value of $dg_2/d\varphi$ and hence on the choice of the potential barrier. At any rate the order of magnitude of $\partial R_L/\partial T$ and $\partial R_L/\partial p$ is correct.

To sum up, the value of the molar refraction of liquid benzene, its dispersion, and its pressure and temperature dependence can be explained by assuming hindered rotation and cybotactic grouping. The characteristic quantities of C_6H_6

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[23] E. N. da C. Andrade, Phil. Mag. **17**, 497 (1934).

[24] J. H. de Boer, Trans. Faraday Soc. **32**, 13 (1936).

[25] P. Pringsheim, *Handbuch der Physik*, Vol. 23/1, p. 246.

are $g_2=0.88$ and $x=1.8$ or $L_z=0.98$ approximately. These quantities can be determined without making any special assumptions concerning the type of grouping or the form of the potential barrier. The assumptions are introduced only to correlate the parameters with quantities which have a simple physical meaning, and to show that their values are reasonable.

The Intensity and Depolarization of the Scattered Light

The theory of the unmodified scattered light for liquids was developed independently by King,[26] Gans[27] and Ramanathan.[28] Free rotation and isotropy of the Lorentz force were assumed. In their original forms the three theories gave different results, but the later papers of Ramanathan and Didlaukies[29] have eliminated these discrepancies. However, the large amount of experimental data available do not verify the theory.[30]

We will follow Ramanathan's general formulation of the theory, but correct it by taking into account the influence of hindered rotation and the anisotropic polarization field. If the incident light of intensity 1 is plane polarized with an electric vector E, the intensity of the light scattered by a unit volume at a distance 1 cm in the direction normal to the plane of E is given by

$$\begin{aligned} I_p&=\tfrac{1}{2}(2\pi/\lambda)^4N[\gamma(\mu_p)_{\mathrm{av}}{}^2+(\mu_p{}^2)_{\mathrm{av}}-(\mu_p)_{\mathrm{av}}{}^2], \\ I_n&=\tfrac{1}{2}(2\pi/\lambda)^4N(\mu_n{}^2)_{\mathrm{av}}. \end{aligned} \tag{16}$$

I_p and I_n are the scattered light components having electric vectors parallel and normal to E, respectively. λ is the wave-length in vacuum, N the number of molecules per cc, $\gamma=NkT\beta$, k Boltzmann's constant and β the isothermal compressibility at the absolute temperature T. μ_p is the component of the induced dipole moment in the direction of E and μ_n is its component normal to E. $(\mu)_{\mathrm{av}}{}^2$ is the square of the average and $(\mu^2)_{\mathrm{av}}$ the average of the square. To find these averages we introduce three Cartesian systems of coordinates (Fig. 5): A fixed system p, n_1, n_2 whose directions coincide, respectively, with E, with the direction of propagation of the incident beam and with the direction of observation. The second system x, y, z has the z axis parallel to the preferred direction of a molecule with the x axis in the plane (pz). The position of this system is given by the angles ϑ, φ. Since the preferred directions are distributed at random the probability of finding a molecule with the preferred axis in the range $d\vartheta$, $d\varphi$ is $\sin\vartheta d\vartheta d\varphi/4\pi$. The third system of coordinates 1, 2, 3 coincides with the axes of the ellipsoid of polarization of the molecule. The orientation of the symmetry axis 1 with respect to the axis z is given by the polar coordinates Θ, ψ, the axis 2 being in the plane ($z1$). The probability that the molecule has this orientation is $\exp(-V/kT)\sin\theta d\theta d\psi/\int\exp(-V/kT)\sin\theta d\theta d\psi$. The field acting on a molecule is given by (9). By calculating successively E_x, E_y, E_z; F_1, F_2, F_3; μ_1, μ_2, μ_3; μ_x, μ_y, μ_z one finds

$$\mu_p=(E+4/3\pi I)\left\{\begin{aligned} &l_x[(b_1\sin^2\theta+b_2\cos^2\theta)\cos^2\psi\sin^2\vartheta+(b_1-b_2)\cos\theta\sin\theta\cos\vartheta\sin\vartheta\cos\psi \\ &\qquad+b_2\sin^2\psi\sin^2\vartheta]+l_z[(b_1\cos^2\theta+b_2\sin^2\theta)\cos^2\vartheta \\ &\qquad\qquad+(b_1-b_2)\cos\theta\sin\theta\cos\vartheta\sin\vartheta\cos\psi], \end{aligned}\right. \tag{17}$$

$$\mu_{n_1}=(E+4/3\pi I)\left\{\begin{aligned} &l_x[(b_1-b_2)\sin\theta\sin\vartheta\cos\psi(\cos\theta\sin\vartheta\cos\varphi-\sin\theta\cos\vartheta\cos\varphi\cos\psi \\ &\qquad+\sin\theta\sin\varphi\sin\psi)-b_2\sin\vartheta\cos\vartheta\cos\varphi] \\ &+l_z[(b_1\cos^2\theta+b_2\sin^2\theta)\sin\vartheta\cos\vartheta\cos\varphi \\ &\qquad+(b_1-b_2)\sin\theta\cos\theta\cos\vartheta(\sin\varphi\sin\psi-\cos\vartheta\cos\varphi\cos\psi)]. \end{aligned}\right. \tag{18}$$

These expressions must be introduced in

$$(\mu_p{}^2)_{\mathrm{av}}=\frac{\int\mu_p{}^2\exp(-V/kT)\sin\theta\sin\vartheta d\theta d\vartheta d\varphi d\psi}{\int\exp(-V/kT)\sin\theta\sin\vartheta d\theta d\vartheta d\varphi d\psi} \tag{19}$$

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[26] L. V. King, Proc. Roy. Soc. **A104**, 333 (1923).

[27] R. Gans, Zeits. f. Physik **17**, 353 (1923).

[28] K. R. Ramanathan, Proc. ind. Assoc. f. cult. sc. **8**, 181 (1923); Indian J. Phys. **1**, 413 (1927).

[29] M. Didlaukies, Ann. d. Physik **5**, 205 (1930).

[30] The difficulties have been discussed by J. Cabannes: *La diffusion moléculaire de la lumière* (Paris, 1929), pp. 204–300.

and the analogous expression for $(\mu_n^2)_{\text{av}}$. $(\mu_p)_{\text{av}}$ is of course identical with the average polarization per molecule I/N and $(\mu_n)_{\text{av}}=0$. The integration of (19) gives

$$(\mu_p^2)_{\text{av}}=[(E+4\pi I/3)^2/15]\begin{cases} l_z^2[b_1^2(2g_2+g_4)+b_2^2(3-5g_2+2g_4)+4b_1b_2(g_2-g_4)] \\ \quad +l_x^2[b_1^2(3-5g_2+2g_4)+b_2^2(3+3g_2+2g_4)+2b_1b_2(1+g_2-2g_4)] \\ \quad +2l_xl_z[2b_1^2(g_2-g_4)+b_2^2(1+g_2-2g_4)+b_1b_2(1-3g_2+4g_4)] \end{cases} \tag{20}$$

$$(\mu_n^2)_{\text{av}}=[(E+4\pi I/3)^2/15]\begin{cases} l_z^2[b_1^2(2g_2-g_4)+b_2^2(1-g_4)+2b_1b_2(g_4-g_2)] \\ \quad +l_x^2[b_1^2(1-g_4)+b_2^2(1+g_2+g_4)+b_1b_2(-1-g_2+2g_4)] \\ \quad +l_xl_z[b_1^2(2g_4-2g_2)+b_2^2(-1-g_2+g_4)+b_1b_2(-1+3g_2-4g_4)] \end{cases} \tag{20$'$}$$

where g_2 and g_4 are the functions of the potential barrier defined in Eq. (2). If we take again $s=\frac{1}{3}$, the definitions (10) give

$$l_x=1/(1+x(1-B)/4),\quad l_z=1/(1-xB),$$

where x and B are defined in (12).

If there is no anisotropy of the Lorentz force, $x=0$, $l_x=l_z=1$, we get the classical relations

$$(\mu_p^2)_{\text{av}}=[(E+4\pi I/3)^2/15][3b_1^2+8b_2^2+4b_1b_2],$$
$$(\mu_n^2)_{\text{av}}=[(E+4\pi I/3)^2/15](b_1-b_2)^2.$$

This is true for any value of g_2 and g_4. Hence hindered rotation alone does not alter the classical theory.

If the incident light is not polarized, one has $I_p'=I_p+I_n$, $I_n'=2I_n$ and hence the total intensity of the scattered light is $I_0=I_p+3I_n$, and its depolarization $\Delta=2I_n/(I_p+I_n)$. By introducing (20) in (16) and using the definitions (12) we get

$$I_0=\tfrac{1}{2}(\pi/\lambda^2)^2((n^2-1)^2/N)\cdot i;$$
$$i=[\gamma-1+(M_1+3M_2)3/5]; \tag{21}$$

$$\Delta=6M_2/[5(\gamma-1)+3(M_1+M_2)], \tag{22}$$

where

$$\begin{aligned} M_1&=(l_z^2m_1+l_x^2m_2 \\ &\qquad +2l_zl_xm_5)(R_0/R_L)^2/(p+2)^2, \\ M_2&=(l_z^2m_3 \\ &\qquad +l_x^2m_4-l_zl_xm_5)(R_0/R_L)^2/(p+2)^2 \end{aligned} \tag{23}$$

and

$$\begin{aligned} m_1&=3+g_2(p^2+4p-5)+2g_4(p-1)^2, \\ m_2&=(3p^2+2p+3)+g_2(-5p^2+2p+3) \\ &\qquad +2g_4(p-1)^2, \\ m_3&=1+2g_2(p^2-p)-g_4(p-1)^2, \\ m_4&=(p^2-p+1)+g_2(1-p)-g_4(p-1)^2, \\ m_5&=(1+p)+g_2(2p^2-3p+1)-2g_4(p-1)^2. \end{aligned} \tag{24}$$

For $x=0$ we obtain the classical relations

$$\Delta=6\delta^2/(5\gamma+7\delta^2)$$

where $\delta^2=(p-1)^2/(p+2)^2=(b_1-b_2)^2/(b_1+2b_2)^2$

and $\qquad i=\gamma+13\delta^2/5,$

which lead to

$$i=6\gamma(1+\Delta)/(6-7\Delta). \tag{25}$$

For the case of an anisotropic Lorentz field it is not possible to retain these relations by introducing for example a quantity analogous to the anisotropy factor δ. In particular Eq. (25) is not justified.[31]

The significance and use of the results can best be illustrated by applying them to benzene. Since $p=0.516$ is given, one constructs first a table of B and m_i for a series of values of g_2. We assume again a potential $V_0(1-\cos^2\theta)$ and obtain for each g_2 the corresponding[32] value of g_4 from Fig. 1. Next one tabulates l_x, l_z and $(R_L/R_0)^2$ as functions of x and g_2 and using (23) gets $M_1(x, g_2)$ and $M_2(x, g_2)$. Finally (21) and (22) serve to find the intensity factor $i(x, g_2)$ and the depolarization $\Delta(x, g_2)$. The results are plotted in Figs. 6 and 7. They are constructed

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[31] The determinations of Avogadro's number from the light scattering in liquids presupposes the validity of Eq. (25). This relation is true only if $3M_1-4M_2=5$. In our theory $(3M_1-4M_2)/5$ is a function of g_2 and x. The calculation for benzene shows that this function is very similar to R_L/R_0 shown in Fig. 4. Its value never deviates much from 1. The fact that the light scattering method has furnished approximate, but not accurate values of Avogadro's number is therefore not an argument against but rather for the anisotropy of the Lorentz force.

[32] Fig. 1 shows that (g_2-g_4) remains almost constant for $V_0/kT<5$ and decreases very slowly for higher potential barriers. We have verified the same behavior for other forms of the potential. Hence for small values of g_2 and also for $g_2=1$ our curves do not depend on the choice of V. Between $g_2=0.8$ and $g_2=0.95$, however, the results vary for different potential barriers.

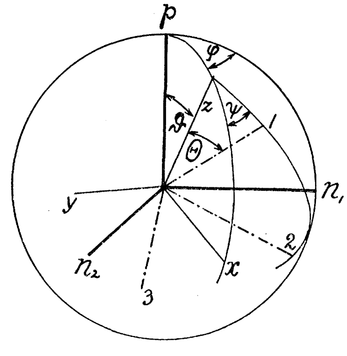

FIG. 5. The 3 coordinate systems used in calculating light scattering and Kerr effect. p, n_1, n_2 is fixed in space; n_1 direction of propagation of incident light; z direction of preferred orientation; 1 momentary direction of symmetry axis of molecule.

with $\gamma = 0.026$, which corresponds to the density and the compressibility of benzene at 18°.

If there were no anisotropy of the Lorentz force we should find $i_0 = 12.0\ 10^{-2}$ and $\Delta_0 = 0.57$ whereas the observations at 15° give[33] $i = 8.2\ 10^{-2}$ and $\Delta = 0.42$. These observed values can be completely understood if $g_2 > 0.8$, as Figs. 6 and 7 show. Our previous results from the refraction, that g_2 is about 0.88 and that x is between 1.4 and 1.8 are thereby given considerable added support.[34]

Recently Turner[35] has shown for benzene that the variation of the intensity of the scattered light with the wave-length is not strictly proportional to $(n^2-1)^2/\lambda^4$. Our theory does not require this proportionality, because i depends on x and hence on R_0 and the wave-length. From $\lambda = 5460$A to $\lambda = 4350$A R_0 increases by about 3 percent, hence x changes by 0.054. For $x = 1.8$, $g_2 = 0.88$ the slope of the curve is about $\partial i/\partial x = 0.2$, hence $\Delta i = (\partial i/\partial x)\Delta x = 0.011$ or an increase of i of about 14 percent. Turner's data give between these wave-lengths an increase of i of about 20 percent.

From the slope of the curves in Fig. 7 it follows that the depolarization should vary by less than 0.01 in the range of the visible spectrum. Within experimental errors of this magnitude the observations have shown no dispersion of the depolarization.

If the potential barrier is low the anisotropy of the Lorentz force gives a larger depolarization than the classical theory. Hence the "apparent" optical anisotropy[36] of the molecules can be larger than for the gas. This will occur in liquids at high temperatures and in gases at high pressures. In fact Rao[37] has shown that near the critical temperature the apparent anisotropy is from 3 to 4 times larger than for the gas, and in gases Volkmann[38] has found an increase of δ^2 with pressure.

Summing up, the theory accounts for all anomalies of the intensity and the depolarization of the scattered light. It is perhaps surprising that the theory of Gans,[27] which is based on statistical considerations, does not lead to our results. This is due to the fact that Gans assumes that the isotropic micro-distribution corresponds to a state of minimum energy. In liquids it seems more natural to assume that in small volume-elements the optical anisotropy fluctuates around a finite value.

THE KERR EFFECT IN LIQUIDS

The measurements of the electro-optical Kerr effect demonstrate the failure of the classical theory of Langevin and Born in the most impressive manner.[39] The Kerr constant K_L of liquids is always much smaller than its theoretical value K_0. The work of Briegleb,[40] and

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[33] Calculated from Cabannes' value $R = 10.7\ 10^{-6}$. Cabannes' remark, that C_6H_6 scatters more than it should, is based on the implication that (25) is correct. (25) gives $i = 7.3\ 10^{-2}$. Actually benzene scatters much less than it should according to the classical theory. Hence we do not think that Rocard's theory can be accepted. See J. Cabannes, *La diffusion moléculaire de la lumière*, pp. 237 and 296.

[34] Figs. 4 and 6 are not appreciably altered if one takes $p = 0.500$ or if a different form of the potential barrier is chosen. The curves in Fig. 7 however are very sensitive to such changes and a better agreement for Δ could not be expected.

[35] A. F. Turner, Diss. University of Berlin (1934), Physik. Ber. **16**, 1860 (1935). The observed increase of i for wave-lengths $\lambda > 5460$A could only be explained if our curves had a large curvature at their minima or if p changes with λ.

[36] The "apparent" optical anisotropy is the value of δ^2 which is obtained from the relation $\Delta = 6\delta^2/(5\gamma + 7\delta^2)$.

[37] R. S. Rao, Ind. J. Phys. **2**, 7 (1924). Rao, Stuart and Volkmann, reference 2, believe that the large increase is not real but caused by experimental difficulties. In view of Volkmann's latest results, reference 38, δ must have a maximum where $\delta^2 > \delta_0^2$.

[38] H. Volkmann, Ann. d. Physik **24**, 457 (1935).

[39] C. V. Raman and K. S. Krishnan, Phil. Mag. **3**, 713 (1927) claim the validity of the classical theory for liquids. But they compare the Kerr constants with the "apparent" anisotropy determined from the depolarization in liquids. Hence their considerations are not a verification of Langevin's theory. They only demonstrate the approximate validity of the relation of Gans between K_L and Δ.

[40] G. Briegleb, Zeits. f. physik. Chemie **14**, 97 (1931); **16**, 249 (1932).

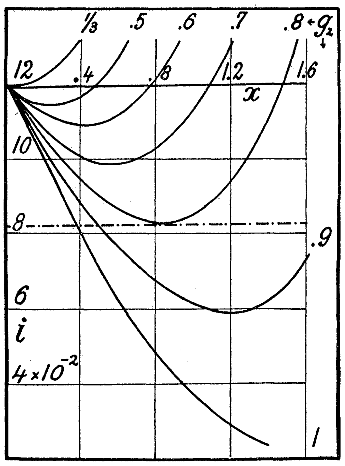

FIG. 6. The intensity factor i for the scattered light for benzene. The dotted line corresponds to the observed value.

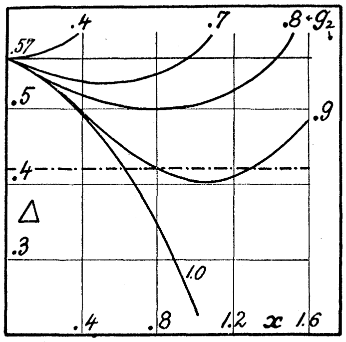

FIG. 7. The depolarization of the scattered light for benzene. The dotted line gives the observed depolarization.

Stuart and Volkmann[2] makes it seem almost impossible to correlate the Kerr constants of liquids with the optical properties of the molecule.

There exist two possibilities for the formulation of a new theory. One might assume that the cybotactic groups behave like small anisotropic crystals. Even if they are spherical they will be oriented by an electric field, and this orientation produces uniaxial birefringence of the liquid. However it can easily be seen that this assumption gives much too large values of the Kerr constant.[41] Although the groups have a smaller optical anisotropy than the molecules, they would orient themselves much more easily, because the energy of orientation is proportional to their volume, while the temperature energy kT is the same as for a single molecule. Supposing the groups contain only 50 molecules and are spherical a calculation carried out on this basis gives for benzene $K_L > 10K_0$, while the experiment gives $K_L < \frac{1}{2}K_0$.

Hence we conclude that the molecules in a quasi-crystalline group are not held together rigidly. Even if the potential barrier is so high that rotation is practically impossible the molecules still have a considerable freedom of translation. They can travel from one preferred position to another. The cybotactic lattice is a rather diffuse structure and does not act like a solid.[42] It is of course possible that the electric field changes somewhat the distribution of the preferred orientations, but we have no experimental data to estimate this effect.[16] It must be small and we shall neglect it altogether.

We calculate therefore the Kerr effect in the usual manner[43] by considering the orienting action of the field on the single molecules. We introduce again the three systems of coordinates (Fig. 5). The axis p is in the direction of the static field E_0 between the plates of the Kerr condenser, n_1 is in the direction of the light beam. The two other systems are defined as in the preceding section. Due to the field E_0 the molecules have an additional potential energy

$$U = \tfrac{1}{2}[a_1F_{01}^2 + a_2F_{02}^2 + a_3F_{03}^2], \tag{26}$$

where a_1, a_2, a_3 are the static polarizabilities of the molecule, F_{01}, F_{02}, F_{03} the components of the Lorentz force of E_0. In the system x, y, z the components of this field are $F_{0x} = f_x(E_0 + 4\pi I_0/3)_x$, where we place $f_x = 1/(1 + x(1 - B_0)/4)$, $f_z = 1/(1 - xB_0)$, $B_0 = [1 - g_2(1 - p_0)]/(p_0 + 2)$, $p_0 = a_1/a_2$, in analogy to the definitions of l_x, l_z, B and p.

For a light wave whose electric vector E_p is parallel to the field E_0 the average polarizability is

$$\gamma_p = \int \mu_p \exp\left(-(V+U)/kT\right) \sin\theta \sin\vartheta\, d\theta\, d\vartheta\, d\varphi\, d\psi \Big/ (E_p + (4/3)\pi I_p) \int \exp\left(-(U+V)/kT\right) \times \sin\theta \sin\vartheta\, d\theta\, d\vartheta\, d\varphi\, d\psi. \tag{27}$$

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[41] If the groups are large and not spherical the Kerr effect turns out to be exceedingly large and has a large relaxation time. This is the case in liquid crystals and in colloids.

[42] This statement does not invalidate our calculation of the Lorentz force, because it can be shown that Ewald's theory is applicable to "diffuse" lattices, in which every atom oscillates about a preferred position.

[43] P. Debye, *Handbuch der Radiologie*, Vol. 6.

μ_p is given by Eq. (17). For a light wave whose electric vector E_n is normal to the field E_0 the average polarizability of a molecule is also given by (27) if we replace μ_p by μ_n where

$$\frac{\mu_n}{(E_n+(4/3)\pi I_n)}=\left\{\begin{aligned}&l_x[(b_1-b_2)\sin\theta\cos\theta\sin\vartheta\cos\varphi(\sin\varphi\sin\psi-\cos\vartheta\cos\varphi\cos\psi)\\&\quad+(b_1\sin^2\theta+b_2\cos^2\theta)(\cos^2\vartheta\cos^2\varphi\cos^2\psi+\sin^2\varphi\sin^2\psi\\&\quad-\cos\vartheta\sin\varphi\cos\varphi\sin\psi(1+\cos\psi))+b_2(\cos^2\vartheta\cos^2\varphi\sin^2\psi+\sin^2\varphi\cos^2\psi\\&\quad+2\cos\vartheta\sin\varphi\cos\varphi\sin\psi\cos\psi)]+l_z[(b_1\cos^2\theta+b_2\sin^2\theta)\sin^2\vartheta\cos^2\varphi\\&\qquad\qquad+(b_1-b_2)\sin\theta\cos\theta\sin\vartheta\cos\varphi(\sin\varphi\sin\psi-\cos\vartheta\cos\varphi\cos\psi)].\end{aligned}\right.$$

The rest of the calculation follows the usual method.[43] One uses $\exp(-U/kT)=1-U/kT$, finds the term proportional to E_0^2, and from $\gamma_p=\gamma+d\gamma_p$ one determines the indices of refraction $n_p=n+dn_p$, $n_n=n+dn_n$, where $dn_p=(4/3)\pi N(n^2+2)^2 d\gamma_p/6n$.[44] The resulting Kerr constant can be written in the usual form

$$K_L=(n_p-n_n)/nE_0^2=(4/3)\pi N[(n^2+2)/2n]^2[(\epsilon+2)/3]^2\Theta_1 \tag{28}$$

but the value of Θ_1 is now given by

$$\Theta_1=1/45kT\left\{\begin{aligned}&l_zf_z^2[a_1b_12g_4+2a_2b_2(1-2g_2+g_4)+a_1b_22(g_2-g_4)+2a_2b_1(g_2-g_4)]\\&\quad-l_xf_z^2[a_1b_1(g_2-g_4)+a_2b_2(1-g_4)+a_1b_2(g_2-g_4)+a_2b_1(1-2g_2+g_4)]\\&\quad-l_zf_x^2[a_1b_1(g_2-g_4)+a_2b_2(1-g_4)+a_1b_2(1-2g_2+g_4)+a_2b_1(g_2-g_4)]\\&\quad+l_xf_x^2[a_1b_12(1-2g_2+g_4)+a_2b_2(1-g_2+g_4)+a_1b_2(-1+3g_2-2g_4)+a_2b_1(-1+3g_2-2g_4]\\&\quad+3l_xf_xf_y[a_1b_1(g_2-g_4)+a_2b_2(g_2-g_4)-a_1b_2(g_2-g_4)-a_2b_1(g_2-g_4)]\\&\qquad\qquad+3l_yf_xf_y[a_1b_1(g_2-g_4)+a_2b_2(g_2-g_4)-a_1b_2(g_2-g_4)-a_2b_1(g_2-g_4)].\end{aligned}\right. \tag{29}$$

n is the index of refraction of the liquid, ϵ its dielectric constant and N the number of molecules per cc. g_2 and g_4 are again the functions of the potential V defined in Eq. (2). If there is no anisotropy of the Lorentz force $x=0$, $l_x=l_z=f_x=f_z=1$ and Eq. (29) reduces to the classical result $\theta_1=(a_1-a_2)(b_1-b_2)2kT/45$. This is true independent of the values of g_2 and g_4. Hence the hindered rotation alone does not alter the classical equation.

For most nonpolar molecules the difference between molar polarization and refraction is small, hence $a_1+2a_2=b_1+2b_2$. If we assume furthermore[45] $p=p_0$, then $f_x=l_x$ and $f_z=l_z$ and the Kerr constant can be written

$$K_L=\frac{4}{3}\pi N\frac{(n^2+2)^2}{6n^2}\cdot\frac{(\epsilon+2)^2}{9}\cdot\frac{(b_1-b_2)^1}{15kT}\cdot\chi, \tag{30}$$

where

$$\begin{aligned}\chi=K_L/K_0=[l_z^3\chi_1+l_x^3\chi_2&\\+l_zl_x(l_x+l_z)\chi_3/2]/(p-1)^2,&\end{aligned} \tag{31}$$

$$\begin{aligned}\chi_1&=1+2(p-1)g_2+(p-1)^2g_4,\\\chi_2&=(p^2-p+1)-(2p^2-3p+1)g_2+(p-1)^2g_4,\\\chi_3&=-(p+1)+(2p^2-5p+3)g_2-2(p-1)^2g_4.\end{aligned} \tag{32}$$

K_0 is the value of the Kerr constant calculated from the classical equation by using the observed values of N, n and ϵ of the liquid and the polarizabilities b_1, b_2 of the molecule as found from measurements in the gas. The theoretical value of χ is a function of x and g_2. This function is plotted in Fig. 8 for benzene, $p=0.516$.

Fig. 8 shows that the Kerr constant depends on the structure of the liquid to a much higher degree than any of the other optical properties. If the potential barrier is small the Kerr constant rapidly increases[46] with the anisotropy of the Lorentz force.

The curves indicate that in liquids the Kerr

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[44] Our expressions for dn_p and dn_n do not satisfy the relation $dn_p/dn_n=-2$, but the deviations are probably too small to be measurable.

[45] This assumption may introduce a quite appreciable error in our results.

[46] No data on compressed gases or liquids near the critical temperature seem to be available. Such measurements would be very valuable. They would furnish the proper interpretation of Rao's results. See reference 37.

effect can be greatly reduced, eventually vanish and even reverse its sign. This marked structure sensitivity of the Kerr constant is confirmed by the experiments of Briegleb.[40]

For $\lambda = 5460\text{A}$ McComb[47] finds for benzene the Kerr-constant $B = Kn/\lambda = 0.63\ 10^{-7}$; Briegleb measured $B = 0.408\ 10^{-7}$. Since all experimental errors tend to reduce B, we shall use the larger value. We find then $K_L = 2.29\ 10^{-12}$ and $K_0 = 5.38\ 10^{-12}$ from the experimental values of n, ρ, ϵ, b_1, b_2. Hence $\chi = 0.426$.

Reference to Fig. 8 shows that this is only possible if again $g_2 > 0.83$. The Kerr effect checks with our previous result that $V_0 = 8.8kT$. Although in this case x appears somewhat smaller than previously this is not serious in view of our assumptions.

A rise of temperature decreases V_0/kT and g_2 and hence increases the value of χ. Since

$$(1/K_L)(dK_L/dT) = (1/K_0)(dK_0/dT) + (1/\chi)(d\chi/dT)$$

we conclude that the negative temperature coefficient of the Kerr constant should be smaller than that given by the classical theory. This is verified by the results of Hansen.[48] His data furnish $(1/K_L)(dK_L/dT) = -1.6\ 10^{-3}$, while we calculate $(1/K_0)(dK_0/dT) = -4.4\ 10^{-3}$. A rough estimate shows that $(1/\chi)(d\chi/dT) = +2.8\ 10^{-3}$ is compatible with the theory.[49]

If one assumes that $(b_1 - b_2)$ is proportional to $(n^2-1)/(n^2+2)$ the classical theory leads to the Havelock relation $Bn\lambda/(n^2-1)^2 = h$, where h is Havelock's constant. According to our theory h must be replaced by $h\chi$. Hence the Havelock "constant" should depend on the wave-length. However this variation is small. For benzene we estimate a change of χ of about 5 percent between $\lambda = 4000\text{A}$ and 6000A. Within experimental errors of this order of magnitude the Havelock relation has been verified.

The classical theory gives a relation between the depolarization of the scattered light and the Kerr constant. This relation of Gans cannot be verified in our theory, because there is no simple relation between M_1, M_2 and χ. Actually for benzene the relation is only approximately correct.

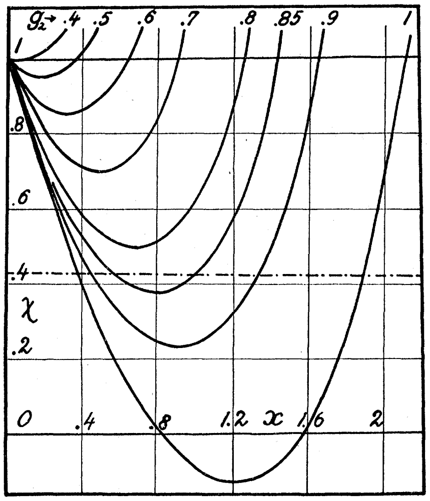

FIG. 8. The Kerr constant for liquid benzene. The dotted line corresponds to the largest observed value.

CONCLUSIONS

The value of the molar refraction of liquid benzene, its dispersion, temperature—and pressure dependence, the intensity and depolarization of the scattered light and its frequency-dependence, the Kerr constant and its temperature and frequency variation, all lead to essentially the same anisotropy of the Lorentz force and the same height of the potential barrier, when interpreted in the light of the present theory. It is probable that still better agreement could be reached by modifying some of our assumptions. Since the potential barrier is very high we must expect that wave-mechanics would give somewhat different curves. A refinement of the theory does not seem worth while before more extensive and more accurate data are available.

It appears then that hindered rotation and cybotactic grouping are sufficient to explain all deviations from the classical theory. The present theory holds only for nonpolar liquids with axial symmetry, but it can be generalized for more complex molecules. For polar molecules it must be modified.

The writer acknowledges the help of Mr. Jakob Leeder in calculating the Lorentz factors for the hexagonal lattice, and is indebted to Dr. A. F. Turner for illuminating discussions concerning the problems of light scattering.

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[47] H. E. McComb, Phys. Rev. 29, 525 (1909).

[48] From Landolt-Börnstein, II. Erg. bd., Vol. 2.

[49] It is probable that in some liquids, especially near the critical temperature, the temperature coefficient of the Kerr effect should be positive.