New electro-optical and magneto-optical effects in liquids

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A brief review is given of the mechanisms responsible for a number of well-known electro-optical and magneto-optical effects, and also the spatial dispersion effects in isotropic (under rotations) liquids. Theoretical estimates and typical experimental values of constants are given. The existence and detection of a number of new electro–optical, magneto-optical, and magneto-electro-optical effects in transparent isotropic liquids are examined. It is indicated which effects are forbidden under left-right reversal symmetry and time-inversion symmetry (no relaxation processes). The mechanisms responsible for many of the effects are considered and the values of the corresponding constants are reproduced. Despite the fact that these constants are small, the effects appear to be measurable through the application of the synchronous detection technique using modulated external electric and magnetic fields.

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INTRODUCTION

The sensitivity of different optical systems for measuring light beam parameters (phase, polarization, and so on) has sharply increased in recent years. This has been achieved, on the one hand, through the use of improved electronics for the detection of signals against background noise and, on the other hand, through the use of light sources of exceedingly high intensity, i.e., lasers. In view of this, we shall review some of the finer effects consisting of changes in the optical properties of transparent isotropic liquids under the influence of external static (or quasistatic) electric and magnetic fields. Let us illustrate the situation by considering the following example.

The well-known optical Faraday effect consists of the rotation of the plane of polarization of light during propagation in a medium and the rate of this rotation is proportional to the amplitude of the externally applied magnetic field H. The question is: why is this effect usually forbidden in the case of an externally applied electric field E and how can this exclusion be removed?

Firstly, the magnetic field H is an axial vector (pseudovector), i.e., its components do not change sign under space inversion. In other words, a definite set of coordinates, for example, a right-handed set, must be used to define H. This also applies to the conventional "angular velocity" $\dot{\varphi}$ with which the plane of polarization rotates. It follows that the linear relationship $\dot{\varphi} = a\mathbf{H}$ does not violate the left-right symmetry. The corresponding constant a is a scalar and is generally nonzero for arbitrary liquids and solids. The electric field E is a true (polar) vector and its components can be defined in either right-handed or left-handed systems. Any linear relationship of the form $\dot{\varphi} = b\mathbf{E}$ that we may obtain will, therefore, violate the left-right symmetry. The pseudoscalar b should be zero for most isotropic liquids. If, however, the liquid contains stereoisomeric molecules in unequal amounts (for example, a solution of "right-handed" sugar), this rule will not work because the liquid itself is not invariant under space inversion.

Secondly, both the magnetic field H and the "angular velocity" $\dot{\varphi}$ change sign under time reversal $t \to -t$. The linear relationship $\dot{\varphi} = a\mathbf{H}$ between them is not, therefore, in conflict with the symmetry of the processes under time inversion. On the other hand, the electric field E does not change sign under time reversal and a relationship of the form $\dot{\varphi} = b\mathbf{E}$ would violate the symmetry of the processes under $t \to -t$. This result may be formulated in a different language, as follows. It will be seen later from the phenomenological form of the permittivity ε_{ik} that the electric analog of the Faraday effect is inconsistent with the well-known principle relating to the symmetry of transport coefficients.[1,2]

However, when an electric field is applied to a liquid, this may result in irreversible processes, e.g., the flow of conduction currents, and this may remove the above rule relating to the $t \to -t$ transformation. In other words, when a current flows through a liquid, its state, although it is stationary, is clearly asymmetric under time reversal and, for such states of a thermodynamic system, the symmetry of the transport coefficients cannot be demonstrated and, in general, is not valid.

The electric analog of the Faraday effect is therefore possible in a liquid, provided the liquid is left-right asymmetric and is capable of conducting electricity. We shall consider below a series of electrooptical and magnetooptical effects in liquids, which seem to us to be

TABLE I.

ε_{ik} (E, H, k)	P	T	Name of effect	Order of magnitude of a_i, cgs esu	Expected phase difference, rad (see text)
$\varepsilon_0\delta_{ik}$	+	+	Refraction	2	
$ia_1e_{ikl}E_l$	−	−	New	$4\cdot10^{-14}$	
$ia_2e_{ikl}H_l$	+	+	Faraday	10^{-10}	10^{-7}
$ia_3e_{ikl}k_l$	−	+	Natural optical activity	$3\cdot10^{-10}$	
$a_4\delta_{ik}E^2$	+	+	Electrostriction	$1,3\cdot10^{-11}$	
$a_5\left(E_iE_k - \frac{1}{3}E^2\delta_{ik}\right)$	+	+	Kerr	$2\cdot10^{-9}$	
$a_6\delta_{ik}H^2$	+	+	Magnetostriction	10^{-18}	
$a_7\left(H_iH_k - \frac{1}{3}H^2\delta_{ik}\right)$	+	+	Cotton-Mouton	10^{-16}	
$a_8\delta_{ik}k^2$	+	+	Only the sum $\varepsilon_0+a_8k^2$ is observable	10^{-15}	
$a_9k_ik_k$	+	+			
$a_{10}\delta_{ik}(EH)$	−	−	New	$4\cdot10^{-22}$	10^{-12}
$a_{11}\left(E_iH_k+H_iE_k - \frac{2}{3}\delta_{ik}(EH)\right)$	−	−	New	$4\cdot10^{-20}$	10^{-10}
$ia_{12}(E_iH_k - H_iE_k)$	−	+	New	10^{-14}	10^{-3}
$a_{13}\delta_{ik}(kE)$	+	−	New	10^{-17}	$5\cdot10^{-6}$
$a_{14}(E_ik_k+k_iE_k)$	+	−	Unobservable	—	
$ia_{15}(E_ik_k - k_iE_k)$	+	+	"	—	
$a_{16}\delta_{ik}(kH)$	−	+	New	10^{-18}	10^{-2}
$a_{17}(H_ik_k+k_iH_k)$	−	+	Unobservable	—	
$ia_{18}(H_ik_k - k_iH_k)$	−	−	"	0	

new. Chapter 2 gives a classification of the possible effects, based on the expansion of the permittivity tensor. In Chapter 3, we shall discuss the mechanisms responsible for the new effects and will estimate the values of the corresponding constants. We shall also consider the possible experimental detection of the new effects.

For completeness, the Appendix summarizes available information on the mechanisms responsible for known optical effects.

EXPANSION OF THE PERMITTIVITY TENSOR

A systematic phenomenological description of effects associated with spatial dispersion, magneto- and electrooptical effects, and similar phenomena is given by Landau and Lifshitz[3] and by Agranovich and Ginzburg.[4] These effects are considered in terms of an expansion of the permittivity tensor $\varepsilon_{ik}(\omega)$ in powers of vectors and tensors characterizing both the light wave itself [wave vector k in the space-time dependence $\exp(-i\omega t+i\mathbf{k}\cdot\mathbf{r})$] and the result of application of external fields to the medium (electric and magnetic fields E and H, velocity gradient $\partial v_i/\partial x_k$, and so on). The essential point is that, in an isotropic liquid, the tensor $\varepsilon_{ik}(\omega)$ can be expressed in terms of other tensors and vectors through the use of only invariant tensors, namely, the Kronecker unit tensor δ_{ik} and the antisymmetric unit pseudotensor e_{ikl}.

We assume that the medium is transparent at the light wave frequency ω and remains transparent when the external fields are applied. The tensor $\varepsilon_{ik}(\omega)$ should then be Hermitian: $\varepsilon_{ik}(\omega)=\varepsilon_{ki}^*(\omega)$. Table I lists expansions of the Hermitian tensor ε_{ik} in terms of the three vectors E, H, k up to quadratic terms, inclusive. All the con-

stants ε_0, a_1-a_{18} are real (for static external fields E and H). Some of the terms proportional to k do not give rise to observable effects for transverse electromagnetic waves (to the first order in the corresponding constant). This is so because the length of the wave vector $|\mathbf{k}|$ for the transverse light wave is not a freely variable parameter but is practically a constant: $|\mathbf{k}| =(\omega/c)\sqrt{\varepsilon_0}$. This is why the refractive index for transverse waves is determined by the sum $\varepsilon_0+a_8k^2$. Moreover, the constants a_9, a_{14}, a_{15}, a_{17}, and a_{18} cannot, in principle, be observed in transverse waves.

The tensor ε_{ik} is a true tensor under inversion of the set of coordinates, the vectors k and E are true (polar) vectors, and H is a pseudovector (axial vector). Accordingly, we assign $P=\pm1$ to the quantities ε_0-a_{18} in such a way that $P=+1$ means that the particular effect may be nonzero in arbitrary liquids, including liquids admitting space inversion, i.e., the left-right transformation. If the liquid is not invariant under inversion, i.e., it "prefers," say, right-handed molecules, the corresponding effect with $P=+1$ will have exactly the same magnitude and sign as for a medium consisting of left-handed molecules. Conversely, an effect with $P=-1$ may differ from zero only for liquids which do not admit inversion. The constant corresponding to an effect with $P=-1$ will then simply change sign under a transformation from a right-handed medium to a left-handed medium.

The presence of parity nonconserving (i.e., left-right asymmetric) terms in the Hamiltonian representing the weak interaction between elementary particles should, in principle, lead to the same type of effect as the left-right asymmetry in the structure of molecules, for example, to optical activity in a gas or liquid consisting of isotropic atoms.[5] Searches for optical activity connected with neutral currents in the weak interaction between the elementary particles are being intensively carried out at present.[6] The situation has been reviewed in the literature[7-9] and the first experimental communications have appeared.[10,11] However, the weak interaction constant is very small, so that optical activity of this kind (effect proportional to a_3 in the table) is at the limit of experimental detection. We shall not, therefore, consider any more complicated (electro- and magnetooptical) effects connected with parity violation in weak interaction.

The behavior of the above vectors and tensors under time reversal must be considered separately. In the region in which the medium is transparent (to the light field), the $t \to -t$ operation corresponds, because of the $e^{-i\omega t}$ factor, to the replacement $\varepsilon_{ik} \to \varepsilon_{ik}^*$. Moreover, $\mathbf{H} \to -\mathbf{H}$, $\mathbf{E} \to \mathbf{E}$, and $\mathbf{k} \to -\mathbf{k}$ under time reversal. Accordingly, we assign one of the two values $T=\pm1$ to each of the terms in the table. In particular, $T=+1$ is assigned to effects for which the corresponding terms transform into themselves with the sign + under the above transformations, and $T=-1$ is assigned to terms that change sign under such transformations.

By virtue of the Hermitian property of the tensor $\varepsilon_{ik} =\varepsilon_{ki}^*$ in the subscripts referring to the light field (no

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absorption at the light frequency), the operation of complex conjugation is equivalent to the interchange of the subscripts in the tensor ε_{ik}. It is easily verified that terms with $T = +1$ in the table satisfy the principle of symmetry of transport coefficients, and those with $T = -1$ are inconsistent with this principle. $T = +1$ means that the effect can occur for thermodynamically reversible processes. For example, when an electric field is applied to a liquid, there is a loss of energy due to the reorientation of the molecules (the term proportional to a_5, Kerr effect, $P = T = +1$), but this energy is returned to the field source when the field is removed.

Conversely, the symbol $T = -1$ indicates that dissipative, i.e., thermodynamically irreversible, processes are essential for the corresponding effect. These irreversible processes can occur in the medium when an electric field is applied to it: for example, conduction currents correspond to the irreversible conversion of electrical energy into heat. We note, by the way, that the presence of a static magnetic field H in the medium and (or) light photons to which the medium is transparent (vector k) cannot give rise to irreversible processes. It follows, in particular, that the constant a_{18} must be zero (it cannot be observed with transverse waves).

In order to resolve the difficulties associated with this relatively unusual situation, i.e., violation of the principle of symmetry of transport coefficients, [1] let us elucidate all this by considering the example of the electric analog of the Faraday effect. Let the electric field in the light wave be $\mathbf{E}(\omega_1)$ and the quasistatic electric field $\mathbf{E}(\omega_2)$. We have explicitly introduced the (small) frequency ω_2 of the quasistatic field, especially since this field will have to be periodically varied when a modulation system is used for observing the effect. The effect proportional to a_1 can then be written as an addition to the induction vector $\mathbf{D}(\omega = \omega_1 + \omega_2)$ in the form

$$D_j\,(\omega = \omega_1 + \omega_2) = \chi_{jkl} E_k\,(\omega_1)\,E_l\,(\omega_2), \quad \chi_{jkl} = i a_1 e_{jkl}.$$

We are therefore dealing with an effect that is nonlinear in the fields. In the most general case, the nonlinear polarizability tensor for the given frequencies ω_1 and ω_2 does not satisfy the symmetry relations in the subscripts j and k. [12,13] It is only in the special case when there is no absorption at the three frequencies ω_1, ω_2, $\omega_1 + \omega_2$ and, moreover, the dependence of χ on ω_2 can be neglected, that one can demonstrate the symmetry of χ_{jkl} in the subscripts jk (this is the so-called Kleinman rule in nonlinear optics). However, it is precisely for electrically conducting fluids that the condition of zero absorption at ω_2 may not be satisfied, even though the fluid may remain transparent at ω_1 and $\omega_1 + \omega_2$.

The violation of the principle of symmetry of transport coefficients in the subscripts referring to the light field for effects that are linear in this field is connected with the following fact. When processes that are asymmetric in time occur in the medium, its state (density matrix) also loses its symmetry under the operation of complex conjugation. In quantum mechanics, this operation describes time reversal. In our case of an electrically conducting liquid, the current state corresponds to an asymmetric (under $t \to -t$) distribution of charged particles in momentum space; the flow of current is then accompanied by thermodynamically irreversible processes involving an increase in entropy. [2]

In order to elucidate once again the foregoing discussion, let us express the quasistatic field $\mathbf{E}(\omega_2)$ in the liquid in terms of the current density $\mathbf{j}$ and the quasistatic conductivity σ, i.e., let us write $\mathbf{E}(\omega_2) = j/\sigma$. The electric analog of the Faraday effect can then be written in the form

$$\delta \varepsilon_{ik} = i\,\frac{a_1}{\sigma}\,e_{ikl} j_l.$$

Since the current $\mathbf{j}$ changes sign under time reversal, this expression for $\delta\varepsilon_{ik}$ may be looked upon as not being in conflict with the principle of symmetry of the kinetic coefficients. However, we prefer not to hide behind this redesignation, and state explicitly the violation of symmetry.

In conclusion of our discussion of the $T = +1$ symmetry, we recall that ultraweak interactions between elementary particles, that can be seen in kaon decays, are known to be parity nonconserving under time reversal (T-odd). The simultaneous violation of T- and P-parity should, in principle, ensure that the electron has a nonzero electric dipole moment d along the spin. The electric analog of the Zeeman splitting of terms with spin parallel and antiparallel to the static electric field should give rise to an electric analog of the Faraday effect in the same way as the usual (magnetic) Zeeman splitting produces the usual Faraday effect. Dissipation processes are then no longer necessary for the appearance of $a_1 \neq 0$.

The current upper limit for d[14] is $d < 10^{-13}\mu_B$, where μ_B is the Bohr magneton. In addition, the estimate for a_1 due to the ultraweak P- and T-parity nonconserving interaction gives rise to an additional factor representing the weakness of the spin-orbital interaction in the atom. The final estimate is $a_1 < 10^{-14} a_2$, which is smaller by 11 orders of magnitude than our prediction of a_1 based on the molecular current mechanism (see below).

In the column headed "name of effect" in the table, we give the established designation or a brief characterization of the mechanism responsible for the effects.

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[1] We have not found in the literature any direct discussion of physical systems for which the principle of symmetry of transport coefficients, written in the form $\varepsilon_{ik}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{H}) = \varepsilon_{ki}(\omega^*, -\mathbf{k}, \mathbf{E}, -\mathbf{H})$, [34] would be violated. We are indebted to V. M. Agranovich, V. L. Ginzburg, and L. P. Pitaevskiǐ, whose remarks have enabled us to recognize better the nontrivial nature of this point.

[2] We note that the presence of "superfluid" or "superconducting" currents in the system also makes the state asymmetric under time reversal $t \to -t$, although thermodynamically irreversible processes do not take place in this case.

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In relation to effects proportional to a_1, a_{10}, a_{11}, a_{12}, a_{13}, and a_{16}, we have taken the liberty of describing the corresponding effects as "new" since we have not found in the literature a description or discussion of them. The effect proportional to a_{13} is analogous to the phenomenon of "dragging" of light by a moving liquid (the Fizeau experiment; see, for example, Sommerfeld[15]). The only difference is that, in our case, this motion involves only a definite component of the liquid (ions of a given sign in solution) and the velocity v of this motion is proportional to the applied field E.

In relation to macroscopic phenomena, the terms proportional to a_1, a_2, a_3, and a_{12} correspond to the rotation of the plane of polarization of light, and two transits of the beam (forward and reverse directions) result in a doubling of the effects proportional to a_1, a_2, and a_{12} but, for the natural optical activity (proportional to a_3), this results in a cancellation of the effect. The terms proportional to a_5, a_7, and a_{11} lead to induced birefringence and to a change in the refractive index averaged over the two polarizations. All three effects are independent of the direction of k and, therefore, accumulate as a result of back and forth transmission. The terms proportional to a_4, a_6, a_{10}, a_{13}, and a_{16} describe simply the change in the refractive index, where the effects proportional to a_4, a_6, and a_{10} are doubled as a result of a double transit (to and fro) whereas those proportional to a_{13} and a_{16} are cancelled out.

The above considerations relating to the P, T properties and macroscopic manifestations of the various effects can be used similarly to discuss the properties and mechanisms of phenomena corresponding to terms that are of higher order in E, H, and k. This also refers to other fields and their gradients in liquids (concentration fields, temperature fields, velocity fields, and so on). Unfortunately, however, fast external modulation of such fields is practically unattainable, and this severely restricts the possibilities of experimental detection.

In the present paper, terms of degree higher than the second in E, H, and k will not be discussed although they appear to include many interesting effects.

ESTIMATES OF THE CONSTANTS FOR NEW EFFECTS

1: The effect proportional to a_1 has as its macroscopic manifestation the exact analog of the Faraday effect with the magnetic vector H simply replaced by the electric field E. For this effect to exist, the liquid must be noninvariant under the transformation of right into left. At first sight, the additional rotation of the plane of polarization proportional to a_1E is practically indistinguishable against a background of fluctuations in the larger rotation proportional to a_3k due to natural optical activity. In general, the latter is always present in such media. There is, however, one point that is favorable for the new effect. Firstly, the "sugar" rotation of the given medium at a given wavelength can be reduced to zero by adding to the liquid (solution) the molecules of another chemical compound with opposite

sign of natural rotation. The medium as a whole will then remain asymmetric under inversion, as before, despite the fact that $a_3 = 0$. Secondly, rotation due to the new effect is doubled as a result of to-and-fro passes (as in the Faraday case), and the "sugar" rotation cancels out even if we do not make sure that a_3 itself is zero. Thirdly, the sign of the constant a_1 must change when all the "right" components of the liquid are replaced by the "left" components, and vice versa. All this may isolate the effect in which we are interested even when the application of the electric field to the medium is accompanied by components of the magnetic field H along the beam that are synchronous with E (such components of H will simulate our effect). Finally, the new effect is linear in E and, therefore, any thermal effects associated with the current flowing through the medium (see below) that are proportional to E^2 cannot mask the new effect.

The new effect proportional to a_1 is assigned $T = -1$, which means that it is basically connected with thermodynamically irreversible processes of dissipation of the energy of the external electric field E in the liquid.

We shall consider below two mechanisms that can be responsible for the appearance of the effect proportional to a_1. Both mechanisms are based on the fact that, under the influence of the external field E, the left-right asymmetric molecules begin to revolve with angular velocity Ω and there is a nonzero $\langle \Omega \rangle = \xi E$, i.e., a nonzero average of this angular velocity over the initial orientations of the molecules. The rotation of the molecules leads to the appearance of Coriolis forces (in the coordinate system attached to the nuclei). These forces have an effect on the motion of the electrons and are, in some ways, analogous to the effect of the Lorentz force due to an effective magnetic field. The order of magnitude of this effective magnetic field can be estimated with the aid of the Larmor theorem: $H_{eff} \sim (2mc/e)\langle \Omega \rangle$. A more rigorous analysis of the question will confirm this estimate. It may therefore be concluded that molecules of this left-right asymmetric component of the liquid are located in an effective magnetic field given by

$$H_{eff} \sim \frac{2\xi mc}{e} E, \tag{1}$$

where ξ is the constant of proportionality between $\langle \Omega \rangle$ and E, i.e., $\langle \Omega \rangle = \xi E$.

We note that a magnetic field produced directly by a charge e rotating with angular velocity Ω at a radial distance $r \sim a$ is of the order of $H_1 \sim M/a^3 = \Omega e/ac$, where $M = ea^2\Omega/c$ is the magnetic moment due to the rotation of the charge and $a \sim 3 \times 10^{-8}$ cm is of the order of the size of the molecule. We thus have

$$\frac{H_1}{H_{eff}} = \frac{e^2}{mc^2} \frac{1}{a} = \frac{r_{cl}}{a} \sim 10^{-5}, \tag{2}$$

where $r_{cl} = 2.8 \times 10^{-13}$ cm is the classical radius of the electron. The contribution of the "Coriolis" field is thus the dominant one.

The first of the two mechanisms responsible for $a_1 \neq 0$ can be realized in a purely static electric field where a

constant current flows through the liquid. Suppose that the liquid contains charged left-right asymmetric ions of density N_i (cm^{-3}). Under the influence of the field E, these ions move with mean translational velocity $\langle v \rangle = \mu E$, where μ is the ion mobility. As a result of the "propeller" effect, these ions will also rotate with a certain angular velocity $\langle \Omega \rangle = b \langle v \rangle$, where the coefficient b has the dimensions of the reciprocal of length and its order of magnitude is $b \sim \psi a^{-1}$, where $\psi \sim 0.1-1$ is a dimensionless coefficient that depends on the hydrodynamic form of the molecule (for example, see Happel and Brenner[16]).

Therefore, $\langle \Omega \rangle = a^{-1} \mu E$. In approximate estimates, the mobility μ is conveniently expressed in terms of the diffusion coefficient D (cm^2/sec) with the aid of the Einstein relation $\mu = eD/kT$. We then have

$$H_{eff}, = \gamma E, \quad \gamma = 2 \frac{mc^2}{kT} \frac{D\psi}{ac}. \tag{3}$$

If we suppose that the Verdet constant per ion is not very different from the corresponding constant of the original molecule, we have

$$a_1 = \frac{N_i}{N_0} a_2 \cdot 2 \frac{mc^2}{kT} \frac{D\psi}{ac}, \tag{4}$$

where a_2 is the macroscopic constant for the Faraday effect in a medium consisting of the above asymmetric molecules of density N_0.

Another mechanism that may produce $a_1 \neq 0$ may be realized in the course of orientation of left-right asymmetric molecules with static dipole moment d_1 in an external alternating electric field. The simple relaxation equation for the "angle" of orientation of the molecule can be written in the form

$$\langle \dot{\varphi} \rangle + \Gamma \langle \varphi \rangle = \Gamma \frac{d_1}{kT} E e^{-i\omega_2 t}, \tag{5}$$

where Γ^{-1} (sec) is the orientation relaxation time and ω_2 is the frequency of the external electric field E (ω_2 corresponds to the radio band). Fabelinskii[17] has given an analysis of the orientation relaxation processes in connection with molecular scattering problems. The solution for $\langle \dot{\varphi} \rangle$ is

$$\langle \dot{\varphi} \rangle = \frac{-i\omega_2}{1-(i\omega_2/\Gamma)} \frac{d_1}{kT} E e^{-i\omega_2 t}. \tag{6}$$

Again, due to the "propeller" effect, we may suppose that

$$\langle \Omega \rangle = \psi' \langle \dot{\varphi} \rangle \frac{E}{E} = \psi' \frac{-i\omega_2}{1-(i\omega_2/\Gamma)} \frac{d_1}{kT} E e^{-i\omega_2 t}; \tag{7}$$

where $\psi' \sim 0.1-1$ is a dimensionless coefficient characterizing the left-right asymmetry of the rotational relaxation of the molecules (see Happel and Brenner[16]). The essential point is that the corresponding molecules need not be dissociated into ions. Denoting their density by N_m, we obtain

$$a_1 = a_2 \frac{N_m}{N_0} \psi' \frac{-i\omega_2}{1-(i\omega_2/\Gamma)} \frac{2d_1 mc}{kTe}. \tag{8}$$

At low frequencies, $\omega_2 \ll \Gamma$, we may write $\delta \varepsilon_{ik} = ie_{ikl} \text{const} \cdot dE_l/dt$, where the real constant (const) is independent of the frequency ω_2 of the rf field and does not contain the relaxation constant Γ. This effect can be assigned $T = +1$. At high frequencies, $\omega \gg \Gamma$, we may write $\delta \varepsilon_{ik} = ie_{ikl} \text{const}' \Gamma E_l$, where the real constant (const') is again independent of Γ and ω_2. The presence of the factor Γ shows once again that $T = -1$, i.e., it emphasizes the role of irreversible processes.

Let us now consider some numerical values. Assuming that $a_2 \sim 10^{-10}$ cgs esu, $N \sim 10^{22}$ cm^{-3}, $N_i/N_0 \sim 10^{-2}$, $\psi \sim 0.1$, $D \approx 10^{-5}$ cm^2/sec, and $T = 300$°K, we find that $a_1 \sim 4 \times 10^{-14}$ cgs esu for the first mechanism. For $E \sim 300$ V/cm, $\lambda_{light} = 0.63 \mu$, the angle of rotation of the plane of polarization over a length $L = 100$ cm is $\sim 10^{-7}$ rad. When the light-beam power is 1 W (5×10^{18} photons/sec) and the quantum efficiency of the photodetector is ~ 0.1, the time required to record this signal against the shot noise background is $\sim 10^{-4}$ sec. The important point is that periodic modulation of the external electric field should enable us to exclude slow instabilities during the angle measurements. In fact, Aleksandrov and Zapasskii[18] have recently described an experiment in which an amplitude of modulation of the angle of rotation of the plane of polarization of $\sim 10^{-8}$ rad could be measured.

For the second mechanism with $\psi' \sim 0.1$, $N_m/N_0 \sim 0.1$, $\omega_2/2\pi \gtrsim \Gamma/2 \gtrsim 10^9$ Hz, and $d_1/e \sim 10^{-8}$ cm, we find that $a_1 \sim 10^{-13}$ esu. It is difficult to determine whether this effect could be observed for $\omega_2/2\pi \sim 10^9$ Hz because it is difficult to avoid accompanying magnetic fields. Moreover, we note that a large rise in the Faraday effect constant [$\propto (\omega - \omega_0)^{-2}$] tends to reinforce our effect as we approach resonance $\omega \to \omega_0$ for either of the mechanisms.

10, 11: The effects proportional to a_{10}, a_{11} have $P = T = -1$. If we consider the above mechanism involving the rotation of the molecule during motion with velocity $\langle v \rangle = \mu E$, we may suppose that $H_{eff} = \gamma E$ and express the constants of the mixed magnetoelectric effects proportional to a_{10}, a_{11} in terms of the purely magnetic effects proportional to a_6, a_7 (magnetostriction and the Cotton-Mouton effect;

$$a_{10} \sim a_6 \cdot 2\gamma \frac{N_i}{N_0}, \quad a_{11} \sim 2\gamma a_7 \frac{N_i}{N_0}, \tag{9}$$

where γ is given by (1) and the constants a_6, a_7 refer to the medium with density N_0. It seems that these effects are difficult to detect. Thus, for the values of a_{10} and a_{11} given in the table for $\lambda \sim 0.6 \mu$, and for the same density as in the case of the effect proportional to a_1, we find that, for $H \sim 1000$ G, $E \sim 300$ V/cm, and $L \sim 100$ cm, the additional advance of phase is $\Delta \varphi_{10} \sim 10^{-12}$ rad, $\Delta \varphi_{11} \sim 10^{-10}$ rad.

12: The effect proportional to a_{12} is, in its macroscopic manifestations, analogous to the Faraday effect with the replacement

$$H_{eff} \propto E \times H \tag{10}$$

Since $T = +1$, $P = -1$, one would expect that this effect is due to a purely electronic mechanism. The order of magnitude of the corresponding constant can be estimated as follows. The addition to the polarizability α (cm³) of a molecule in the first order in the dipole-interaction Hamiltonians $\mathbf{d} \cdot \mathbf{E}$ and $\boldsymbol{\mu} \cdot \mathbf{H}$ for electrons interacting with electric and magnetic fields, respectively, is

$$\delta\alpha \sim \alpha \frac{d_0 E}{\hbar\omega_{\text{at}}} \frac{\mu_B H}{\hbar\omega_{\text{at}}}, \tag{11}$$

where $d_0 \sim ea$ is of the order of the matrix element of the dipole moment for the transitions in the molecule, μ_B is the Bohr magneton, and $\hbar\omega_{\text{at}}$ is the characteristic "atomic" binding energy. In the estimate for the constant a_2 in the case of the Faraday effect, we again have the parameter $\mu_B H/\hbar\omega_{\text{at}}$ (see the Appendix). Moreover, $d_0/\hbar\omega_{\text{at}} \sim E_{\text{at}}^{-1} \sim (10^7 \text{ esu})^{-1}$, where E_{at} is the characteristic electric field in the molecule. From (11), we therefore obtain the following estimate for the constant a_{12}:

$$a_{12}^{\text{elec}} \sim a_2 \frac{1}{E_{\text{at}}} \sim 10^{-17} \text{ cgs esu.} \tag{12}$$

Moreover, there is also an orientational mechanism for $a_{12} \neq 0$. In the presence of a magnetic field $\mathbf{H}$, the polarizability tensor of an individual molecule at the light frequency must be increased by

$$\delta\alpha_{ik} = ie_{ikm}\rho_{ml}H_l, \tag{13}$$

where the tensor ρ_{ml} depends on the orientation of the molecule. Averaging over the completely random distribution of the orientations of the molecules gives $\delta\varepsilon_{ik} = ie_{ikl}H_l a_2$, i.e., the Faraday effect. If, however, the molecule is not left-right symmetric and has a static dipole moment d_1, then averaging over the angles in the presence of the electric field $\mathbf{E}$ gives rise to the additional term

$$\delta\varepsilon_{ik} \sim a_2 i (H_i E_k - E_i H_k) \frac{d_1}{kT}; \tag{14}$$

where the dimensionless parameter $d_1 E/kT$ characterizes the change in the Boltzmann distribution of the molecules over the orientations in the first order in the electric field $\mathbf{E}$. Moreover, under these conditions, $a_{12} \sim a_2 d_1/kT$. Symbolically,

$$a_{12}^{\text{elec}} : a_{12}^{\text{orient}} \sim kT : \hbar\omega_{\text{at}}. \tag{15}$$

Numerical estimates give the following results for the orientational mechanism:

$$a_{12}^{\text{orient}} \sim 10^{-14} \text{ cgs esu.}$$

To observe the effect, one must use electric and magnetic fields with components at right-angles to the beam. Assuming that $H \sim 1000$ G, $E \sim 3000$ V/cm, $\lambda = 0.63\ \mu$, and cell length $l = 100$ cm, we find that the angle of rotation of the plane of polarization is $\varphi \sim 0.001$ rad for the orientational mechanism. This type of modulation

in the position of the plane of polarization is quite easily detectable (see above) and one would therefore hope that this effect will soon be detected. Moreover, there are reasons to expect that, in the isotropic phase of a material close to the transition into the liquid-crystalline state, the constant a_{12} will be substantially higher due to the easier orientation of the molecules.

13: The effect proportional to a_{13} has $P = +1$, $T = -1$ and is analogous to the dragging of light by a moving liquid (see, for example, Sommerfeld[15]). The motion of a definite ion component in the electrolyte due to the application of an external quasistatic electric field is important for our purposes. We then have $\delta\varepsilon \sim (N_i/N_0) \times (\partial\varepsilon/\partial\omega)\mathbf{k}\langle\mathbf{v}\rangle$ and, as before, $\langle\mathbf{v}\rangle = eDE/kT$. Substituting $(\partial\varepsilon/\partial\omega) \sim \varepsilon/\omega$, $N_i/N_0 \sim 0.01$, we find that $a_{13} \sim 10^{-17}$ cgs esu. For $l = 100$ cm, $E = 300$ V/cm, and $\lambda = 0.6\ \mu$, we obtain an advance of phase of $\sim 5 \times 10^{-6}$ rad. The effect should increase rapidly as compared with this estimate when the frequency of the radiation approaches the frequency of a resonance transition in the ion.

16: The effect proportional to a_{16} may be present in a P-odd medium when the processes taking place are reversible. The purely electronic mechanism yields the simple estimate

$$a_{16} \sim a_2 \frac{\mu_B}{\hbar\omega_{\text{at}}} \sim a_2 a \sim 10^{-18} \text{ cgs esu.} \tag{16}$$

The effect appears to be accessible to observation in refractometers of special design, for example, in a Rayleigh interferometer. Thus, for $H \sim 1000$ G and cell length $l \sim 1$ m, the additional advance of phase, which is proportional to H, is 0.01 rad. A modulation of this order in the phase difference between two interfering beams can readily be observed by modern methods.

APPENDIX: ESTIMATES OF CONSTANTS OF KNOWN PHYSICAL EFFECTS

For completeness, we now reproduce information on the leading mechanisms of known electrooptical, magnetooptical, etc., effects and the magnitudes of the corresponding constants. All the values of the constants are given in electrostatic units.

0: The permittivity of liquids in the optical band is determined by the deformation of the electron shells of molecules under the action of the light field. Assuming that the light field frequency ω is well removed from the frequency ω_0 of the main electronic transitions, we find that the polarizability of the molecule α[3] is given by $\langle d \rangle = \alpha E \sim d_0(d_0 E/\hbar\omega_0)$, where E is the light field, $d_0 = ea_B$ is the characteristic magnitude of atomic-molecular matrix elements of the dipole moment, and a_B is the Bohr radius. The dimensionless parameter $(d_0 E/\hbar\omega_0)$ is the ratio of the dipole-interaction Hamiltonian $\mathbf{d} \cdot \mathbf{E}$ to the characteristic molecular energy differences $\hbar\omega_0$. The final results are: $\alpha \sim a_B^3 \approx 10^{-24}$ cm³ and $\varepsilon = 1 + 4\pi N\alpha \approx 2$ for $N \approx 10^{23}$ cm⁻³.

2: The Faraday effect corresponds to the modification of the polarizability in the first order in the magnetic field H. Assuming that the dipole Hamiltonian is $\sim \mu_B H$, where μ_B is the Bohr magneton, we have $\delta\alpha$

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$\sim \alpha_0 (\mu_B H/\hbar\omega_0)$. More rigorous analysis will show that, for $\omega \ll \omega_0$, there is an additional factor[3] of order $2\omega/(\omega_0 - \omega)$ which, under typical conditions, amounts to about $\frac{1}{3} - \frac{1}{5}$ and is unimportant for numerical estimates. The rotation of the plane of polarization over a path L is $\varphi = (2\sqrt{\varepsilon_0})^{-1} L\omega H a_2 \cos\theta/c = VHl\cos\theta$, where $\sqrt{\varepsilon_0}$ is the refractive index, θ is the angle between $\mathbf{H}$ and $\mathbf{k}$, and V is the Verdet constant. Typical values for nonferromagnetic media are: $V \approx 4.47 \times 10^{-6}$ rad/G$\cdot$cm, $a_2 \approx 1.04 \times 10^{-10}$ cgs esu for density $N \approx 3.34 \times 10^{22}$ cm^{-3} (the experimental values are given for H_2O and the wavelength of light is 0.546 μ).

3: Natural optical activity described by the term proportional to a_3 is realized only for molecules that are asymmetric under the transformation from the right-handed system of coordinates to the left-handed system. The angle of rotation of the plane of polarization is $\varphi = 0.5 l a_3 (\omega/c)^2$. The estimated addition to the polarizability of an individual molecule, including only the first term in the expansion in powers of a/λ (a is the typical linear size of the molecule), yields $\delta\alpha \sim \alpha_0 ka$. The value of a_3 is proportional to the density N (cm^{-3}) of the optically active molecules in the medium. For saccharose in water and $\lambda = 0.589$ μ, we have $a_3/N \approx 1.16 \times 10^{-32}$ cm$^4 \cdot$ rad, $\varphi/Nl \approx 3.76 \times 10^{-21}$ deg$\cdot$cm$^2 = 6.58 \times 10^{-23}$ rad$\cdot$cm^2, etc.

4: The change in the refractive index proportional to the square of the static electric field, E^2, may be due to two mechanisms. Firstly, there is the purely electronic mechanism involving a modification of the electron shells in the second order in E. In this case, $\delta\alpha \sim \alpha_0 (d_0 E/\hbar\omega_0)^2 \sim \alpha_0 E^2/E_{at}^2$, where E_{at} is the intraatomic (or intramolecular) field which is of the order of 10^7 esu. The corresponding value of a_4 is $a_4 \approx (\varepsilon_0 - 1)/E_{at}^2 \sim 10^{-13} - 10^{-14}$ cgs esu (this should be compared with the self-focusing constant $\varepsilon_2 = 10^{-13}$ cgs esu for glass[20]; if the dependence of a_4 on the frequency ω has been neglected, than $\varepsilon_2 = a_4$). Secondly, we have electrostriction, i.e., the pulling of polarized molecules into a region of higher static field. Under these conditions,

$$\delta\varepsilon = \frac{\partial\varepsilon}{\partial\rho}\delta\rho = \frac{\partial\varepsilon(\omega)}{\partial\rho}\frac{\partial\rho}{\partial p}\frac{\rho}{8\pi}\left(\frac{\partial\varepsilon_0}{\partial\rho}\right)E^2,$$

where $\partial p/\partial\rho$ is the square of the velocity of sound, ρ is the density, and p is the pressure. The value of a_4 for carbon disulfide is approximately 1.3×10^{-11} cgs esu for this mechanism. We note that the ratio of the strictional to the electronic values of a_4 is approximately equal to $(\varepsilon_0 - 1)E_{at}^2/8\pi\rho v^2$, which is $\hbar\omega_0/kT$ for rarefied gases and approximately equal to unity for condensed media.

5: Birefringence proportional to $\mathbf{E}^2$ is the Kerr effect. In addition to the purely electronic mechanism (for which $a_5 \sim a_4$), there is the mechanism involving a change in the orientation of anisotropically polarized molecules. If the molecule (for example, nitrobenzene) has a static dipole moment d_1, then $\delta\alpha \sim (d_1 E/kT)^2 \alpha_{an}(\omega)$, where $\alpha_{an}(\omega)$ is the anisotropic part of the optical polarizability and the dimensionless parameter $(d_1 E/kT)^2$ corresponds to the perturbation of the Boltzmann distribution of the molecules over the angles in second order in the Hamiltonian $\mathbf{d}_1 \cdot \mathbf{E}$. For molecules with zero dipole moments (for example, CS_2), we have $\delta\alpha \sim (\alpha_{an}(0)\mathbf{E}^2/kT)\alpha_{an}(\omega)$, where $\alpha_{an}(0)$ is the anisotropic part of the static polarizability and the parameter $[\alpha_{an}(0)\mathbf{E}^2/kT]$ corresponds to the first-order perturbation due to the Hamiltonian $1/2\alpha_{an}\mathbf{E}^2$. The values of a_5 for $T \sim 300\,°K$ are: $a_5 \approx 6.7 \times 10^{-9}$ cgs esu for nitrobenzene, and $a_5 \approx 6.5 \times 10^{-11}$ cgs esu for CS_2. These values are higher by factors of between 10 and 100 than for most liquids (for nitrobenzene and, especially, CS_2, $\alpha_{an}/\alpha_0 \sim 1$ and, at the same time, the nitrobenzene molecules have nonzero dipole moments). The phase difference for the two orthogonal polarizations in the transverse electric field is given by

$$\varphi = \frac{1}{2\sqrt{\varepsilon_0}}\frac{\omega}{c}lE^2 a_5 = \frac{Q}{\lambda}E^2 l,$$

where λ is the wavelength of light in vacuum. In terms of mixed units for which $[Q] = $cm^2/V^2, we have $Q(CS_2) \approx 1.4 \times 10^{-15}$ cm^2/V^2, $Q(C_6H_5NO_2) \approx 1.5 \times 10^{-13}$ cm^2/V^2. When $\omega \ll \omega_0$, the constant Q should be relatively independent of the wavelength. We note, by the way, that when $\alpha_{an} \sim \alpha_0$,

$$a_5(\text{elec}) : a_5(\text{nondipol}) : a_5(\text{dipol}) \propto \left(\frac{d_0}{d_1}\right)^2 \left(\frac{kT}{\hbar\omega_0}\right)^2 : \left(\frac{d_0}{d_1}\right)\left(\frac{kT}{\hbar\omega_0}\right) : 1.$$

6: The change in the refractive index proportional to H^2 may be due to an electronic mechanism and magnetostriction. In this sense, the constant a_6 is analogous to a_4 multiplied by the factor $(\mu_B/d_0)^2 \sim (e^2/\hbar c^2)^2 \sim 10^{-5}$. The same factor gives the ratio of the diamagnetic polarizability to the dielectric polarizability. Thus, $a_6 \sim a_4(e^2/\hbar c)^2$. The table lists $a_6 \approx 2 \times 10^{-17}$ for CS_2.

7: Similarly, for birefringence proportional to H^2 (Cotton–Mouton effect), we have $a_7 \sim a_5(e^2/\hbar c)^2$. If the path difference is $\varphi = Q'\lambda H^2 l/\lambda$, then for $C_6H_5NO_2$ we have $Q' \approx 9.2 \times 10^{-16}$ G^{-2} and Q' should not be a rapidly varying function of the wavelength.

[1] L. Onsager, Phys. Rev. **37**, 405; **38**, 2265 (1931).
[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Part 1, Nauka, M., 1976 (English Transl., Pergamon Press, Oxford).
[3] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Fizmatgiz, M., 1959 (English Transl., Pergamon Press, Oxford).
[4] V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoi dispersii i teoriya éksitonov (Crystal Optics With Spatial Dispersion and the Theory of Excitons), Nauka, M., 1965.
[5] Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **36**, 964 (1959) [Sov. Phys. JETP **9**, 682 (1959).
[6] M. A. Bouchiat and C. C. Bouchiat, Phys. Lett. B **48**, 111 (1974).

[3] The presence of an odd power of the light wave frequency ω is obvious from the presence of the purely imaginary unit in front of i. Moreover, we are discussing the so-called "diamagnetic" part of the Faraday effect and will neglect the "paramagnetic part."[19]

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[7]V. A. Alekseev, B. Ya. Zel'dovich, and I. I. Sobel'man, Usp. Fiz. Nauk **118**, 385 (1976) [Sov. Phys. Usp. **19**, 207 (1976)].

[8]A. N. Moskalev, R. M. Ryndin, and I. B. Khriplovich, Usp. Fiz. Nauk **118**, 409 (1976) [Sov. Phys. Usp. **19**, 220 (1976)].

[9]F. E. Close, Nature **264**, 505 (1976).

[10]D. C. Soreide *et al.*, Phys. Rev. Lett. **36**, 352 (1976).

[11]P. E. Baird *et al.*, Nature **264**, 528 (1976).

[12]N. Bloembergen, Nonlinear Optics, Benjamin, New York, 1965 (Russ. Transl., Mir, M., 1966).

[13]S. A. Akhmanov and R. V. Khokhlov, Problemy nelineĭnoĭ optiki (Problems in Nonlinear Optics), VINITI, M., 1964.

[14]P. G. H. Sandars, in: Atomic Physics, ed. by G. zu Pulitz, E. W. Weber, and A. Winnacker, Vol. 4, Plenum Press, New York, 1975, p. 71.

[15]A. Sommerfeld, Optics, Academic Press, 1964 (Russ. Transl. IL, M., 1953).

[16]J. Happel and H. Brenner, Low Reynolds Number Hydrodynamics, Prentice-Hall, N.Y., 1965 (Russ. Transl., Mir, M., 1976).

[17]I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Scattering of Light), Nauka, M., 1965.

[18]E. B. Alekdandrov and V. S. Zapasskiĭ, Opt. Spektrosk. **41**, 855 (1976) [Opt. Spectrosc. (USSR) **41**, 502 (1976)].

[19]M. V. Vol'kenshteĭn, Molekulyarnaya optika (Molecular Optics), Gostekhizdat, M., 1951.

[20]M. A. Duguay, I. W. Hansen, and S. E. Shapiro, IEEE J. Quantum Electron. QE-6, 725 (1970).