On the classical theory of molecular optical activity

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Abstract

The basic principles of classical and semi-classical theories of molecular optical activity are discussed. These theories are valid for dilute solutions of optically active organic molecules. It is shown that all phenomena known in the classical theory of molecular optical activity can be described with the use of one pseudo-scalar which is a uniform function of the incident light frequency ω. The relation between optical rotation and circular dichroism is derived from the basic Kramers-Kronig relations. In our discussion of the general theory of molecular optical activity we introduce the tensor of molecular optical activity. It is shown that to evaluate the optical rotation and circular dichroism at arbitrary frequencies one needs to know only nine (3 + 6) molecular tensors. The quantum (or semi-classical) theory of molecular optical activity is also briefly discussed. We also raise the possibility of measuring the optical rotation and circular dichroism at wavelengths which correspond to the vacuum ultraviolet region, i.e. for $\lambda \leq 150\ nm$.

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I. INTRODUCTION

In this study we discuss the classical theory of molecular optical activity. This theory was originally developed for solutions of various optically active organic molecules. Our analysis begins with the classical theory of optical activity based on the Maxwell's equations for electromagnetic fields. Any optical active substance is described in this theory with the use of a few phenomenological parameters. The main goal of the classical theory of optical activity is to derive some useful relations between these parameters in various cases. In general, these parameters also depend upon frequencies and relations between such parameters take different forms for different frequencies. We also consider semi-classical theory of optical activity of molecules which was originally developed by Rosenfeld in [1]. In this theory all molecules are considered as quantum systems, while radiation is considered classically. This old theory is still widely used, since it produces a very good agreement with many experimental results. In particular, the semi-classical theory of optical activity can be used at short and very short wavelengths, e.g., for wavelengths which correspond to vacuum ultraviolet. On the other hand, it is clear that the complete theory of optical activity can be based only on quantum mechanics of molecules and quantum theory of radiation.

This work has the following structure. Basics of the classical theory of molecular optical activity in dilute solutions of organic substances can be found in the next Sections. Here we introduce the optical rotatory parameter β. The four Stokes parameters are defined in Section III. These parameters are very convenient to describe quasi-monochromatic light. The phenomenon of circular dichroism is described in Section IV. It appears that the two fundamental $\omega-$dependent functions (optical rotation and circular dichroism) which can be defined for an arbitrary optically active solution can be written in the form of one complex function. The well known Kramers-Kronig relation between the real and imaginary parts of this functions must always be obeyed. For limited intervals of frequencies this produces a very useful relation which allows to determine, e.g., the circular dichroism by using the known expressions for optical activity. Tensor of molecular optical activity is explicitly defined in Section V. The formulas obtained in this Section are very useful in applications, since they allow to express the optical activity by using only the two basic molecular properties (the electric dipole and magnetic dipole momenta). Concluding remarks can be found in the last Section.

II. CLASSICAL THEORY OF MOLECULAR OPTICAL ACTIVITY

Let us briefly discuss the classical theory of optical activity. In classical theory the optical activity always denotes the ability of the material under study to rotate the plane of polarization of the left- and right-circularly polarized light. Currently, the study of optical activity also includes optical rotation at different wavelengths, circular dichroism, and differential scattering of left- and right-circularly polarized light. All these phenomena are manifestations of natural optical activity which is a characteristic of chiral molecules (in contrast with achiral or non-active molecules). Note that there are also various phenomena which correspond to so-called induced optical activitivies. In such cases the achiral molecules can show some optical activity, if, e.g., they are placed in a relatively strong electric and/or magnetic fields. In this study we restrict ourselves to the analysis of the natural optical activity only.

In general, the optical activity is uniformly related to the spatial dispersion, i.e. to the non-local relation between the electric induction $\mathbf{D}$ and electric field $\mathbf{E}$. For the Cartesian components of these vectors we can write [2]

$$D_i(\mathbf{r}, t) = E_i(\mathbf{r}, t) + \int_0^\infty d\tau \int d^3\mathbf{r}_1 F_{ij}(\tau, \mathbf{r}, \mathbf{r}_1) E_j(t - \tau, \mathbf{r}_1) \tag{1}$$

where $F_{ik}(\tau, \mathbf{r}, \mathbf{r}_1) = F_{ki}(\tau, \mathbf{r}_1, \mathbf{r})$ is the kernel of integral operator. For monochromatic field components $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \exp(-\imath \omega t)$ and Eq.(1) takes the form

$$D_i(\mathbf{r}) = E_i(\mathbf{r}) + \int d^3\mathbf{r}_1 f_{ij}(\omega; \mathbf{r}, \mathbf{r}_1) E_j(\mathbf{r}_1) \tag{2}$$

This equation with the kernel $f_{ij}(\omega; \mathbf{r}, \mathbf{r}_1)$ expresses a non-local relation between $\mathbf{D}$ and $\mathbf{E}$ which is also called spatial dispersion. In general, the kernel $f_{ij}(\omega; \mathbf{r}, \mathbf{r}_1)$ in Eq.(2) rapidly decreases with interatomic distances. In many cases such a kernel is very small already at distances $\approx 3\, a$, where a designates some average (or effective) atomic dimension. Briefly, the relation, Eq.(2), is written in the form

$$D_i(\mathbf{r}) = \int d^3\mathbf{r}_1 \cdot \epsilon_{ij}(\omega; \mathbf{r}, \mathbf{r}_1) E_j(\mathbf{r}_1) \tag{3}$$

where ϵ_{ij} is some non-local operator (tensor) which also depends upon the frequency ω (see below). The 3×3 tensor $\hat{\epsilon} = \epsilon_{ij}$ is the dielectric tensor (also called electric permittivity). From the transparency of the media it follows that all nine matrix elements ϵ_{ij} are real and all three eigenvalues of this tensor are positive.

In all studies of optical activity in organic compounds only infinite, homogeneous media are considered, a convention adopted in this work. Unless otherwise specified, the absorption of radiation is assumed to be absent at all frequencies considered below. In such cases the kernel in Eq.(2) depends only on the difference $\mathbf{R} = \mathbf{r} - \mathbf{r}_1$. The functions $\mathbf{D}$ and $\mathbf{E}$ in infinite, homogeneous media can be expanded in a Fourier integral with the respect to Cartesian coordinates as well as time. Finally, this allows one to obtain the following relation between the corresponding Cartesian components of the vectors $\mathbf{D}$ and $\mathbf{E}$

$$D_i(\mathbf{k}) = \epsilon_{ij}(\omega; \mathbf{k})E_j(\mathbf{k}) = \left[\delta_{ij} + \int_0^\infty d\tau \int d^3\mathbf{R} f_{ij}(\tau, \mathbf{R}) \exp[\imath(\omega\tau - \mathbf{k} \cdot \mathbf{R})]\right] E_j(\mathbf{k}) \qquad (4)$$

In other words, the dielectric tensor $\epsilon_{ik}(\omega; \mathbf{k})$ (also called electric permittivity) takes the form

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} + \int_0^\infty d\tau \int d^3\mathbf{R} f_{ij}(\tau, \mathbf{R}) \exp[\imath(\omega\tau - \mathbf{k} \cdot \mathbf{R})] \qquad (5)$$

As follows from this formula the dielectric tensor is a function of the field frequency ω and wave vector $\mathbf{k}$. In general, the dependence of the dielectric tensor ϵ_{ij} on ω is called dispersion, while the analogous dependence upon the wave vector $\mathbf{k}$ represents the spatial dispersion. The spatial dispersion of $\epsilon_{ij}(\mathbf{k})$ is responsible for optical activity (see below).

In solutions of organic substances the optical activity corresponds to the case of weak spatial dispersion, i.e. $k = |\mathbf{k}|$ is small. In such cases the tensor $\varepsilon_{ij}(\omega, \mathbf{k})$ can be expanded in powers of the wave vector $\mathbf{k}$, e.g.,

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}^{(0)}(\omega) + \gamma_{ijl}(\omega)k_l + \beta_{ijlm}(\omega)k_l k_m + \alpha_{ijlmn}(\omega)k_l k_m k_n + \ldots \qquad (6)$$

Such an expansion is valid, if the first term in Eq.(6), i.e. $\epsilon_{ij}^{(0)}(\omega)$, has no zeros in a given range of frequencies ω. Since in this study we restrict ourselves to the consideration of transparent (or slightly absorbing) solutions only, then we can neglect the imaginary part of dielectric tensor $\epsilon_{ij}^{(0)}(\omega)$.

If these two conditions are obeyed, then for small $\mathbf{k}$ only the first few terms in such an expansion are important. Let us restrict to the two lowest order terms (the second of which is responsible for optical activity), i.e. we can write

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}^{(0)}(\omega) + \gamma_{ijl}(\omega)k_l = \epsilon_{ij}^{(0)}(\omega) + \imath \frac{\omega}{c}\gamma_{ijl}(\omega)n_l \qquad (7)$$

where $\mathbf{n} = \frac{c}{\omega}\mathbf{k}$ and $\gamma_{ijl}n_l$ is an antisymmetric tensor of the second rank (upon indexes i and j). For tensor γ_{ikl} the antisymmetry means $\gamma_{ijl} = -\gamma_{jil}$. If absorption of radiation is absent,

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then the tensor γ_{ijl} is real, i.e. $\gamma_{ijl}^* = \gamma_{ijl}$. These two conditions mean that the $\gamma_{ijl}n_l$ tensor can be re-written into another form $\gamma_{ijl}n_l = \frac{c}{\omega}e_{ijl}g_l$, where e_{ijl} is the complete antisymmetric tensor, while g_l is the $l-$th component of the axial giration vector $\mathbf{g}$. In tensor algebra this relation is called the duality relation. In general, the giration vector $\mathbf{g}$ is a function of the unit wave vector $\mathbf{n}$, i.e. $(\mathbf{g})_i = g_{il}n_l$, where g_{il} is the pseudotensor of the second rank. In isotropic media $g_{il} = \delta_{il}f$ and such a pseudotensor is reduced to a single pseudoscalar f. In this case the γ_{ijl} tensor is essentially reduced to the complete antisymmetric tensor e_{ijl}.

In fact, for the tensor γ_{ijl} one finds $\gamma_{ijl}(\omega) = \frac{c}{\omega}e_{ijl}f(\omega)$, and therefore,

$$\mathbf{D} = \epsilon^{(0)}\mathbf{E} + \imath f(\omega)(\mathbf{E} \times \mathbf{n}) \tag{8}$$

Note again that this equation can be applied only in those cases when the absolute value of $f(\omega)$ is much smaller than the minimal eigenvalue of the tensor $\epsilon^{(0)}(\omega)$.

As is well known (see, e.g., [2]) in an arbitrary dielectric media we always have $\mathbf{D} \cdot \mathbf{n} = 0$. In this case from Eq.(8) one also finds that $\mathbf{E} \cdot \mathbf{n} = 0$. For a monochromatic wave we can write the Maxwell equations

$$\frac{\omega}{c}\mathbf{H} = (\mathbf{k} \times \mathbf{E}) \quad and \quad \frac{\omega}{c}\mathbf{D} = (\mathbf{k} \times \mathbf{H}) \tag{9}$$

It follows from here that $\mathbf{k} \perp \mathbf{D} \perp \mathbf{H}$ and also that $\mathbf{E} \perp \mathbf{H}$. In three-dimensional space this means that the three vectors $\mathbf{E}, \mathbf{D}$ and $\mathbf{k}$ are coplanar. This simplifies drastically the following analysis of optical activity in isotropic media.

Consider now the energy transfer. In general, the direction of the energy flux is given by Poynting vector $\mathbf{S} = \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H})$. Now by using the unit vector $\mathbf{n}$ defined above ($\mathbf{n} = \frac{c}{\omega}\mathbf{k}$) we can write for the Poynting vector

$$\mathbf{S} = \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H}) = \frac{c}{4\pi}[\mathbf{n}E^2 - (\mathbf{E} \cdot \mathbf{n})\mathbf{E}] \tag{10}$$

The total energy flux through an element dS of surface orthogonal to $\mathbf{n}$ is

$$dW = \frac{c}{4\pi}[E^2 - (\mathbf{E} \cdot \mathbf{n})^2]d\Omega = \frac{c}{4\pi}E^2 sin^3\Theta d\Theta d\Phi \tag{11}$$

where Θ is the angle between the vector $\mathbf{E}$ and outer normal to this surface element dS, i.e. $\mathbf{n}$. Also, it follows from the two equations of Eq.(9) that $\mathbf{D} = n^2\mathbf{E} - \mathbf{n}(\mathbf{n} \cdot \mathbf{E})$. On the other hand the basic relation between vectors $\mathbf{D}$ and $\mathbf{E}$ is $\mathbf{D} = \hat{\epsilon}\mathbf{E}$, where $\hat{\epsilon}$ is the dielectric tensor. From here one finds the following equation written in Cartesian components

$$(n^2\delta_{ij} - n_i n_j - \epsilon_{ij})E_j = 0 \tag{12}$$

where ϵ_{ij} are the components of dielectric tensor.

Formally, this equation coincides with the corresponding eigenvalue equation for the dielectric tensor ϵ_{ik}. However, the eigenvalues of this tensor are the functions of three spatial directions. By using some unitary transformation, one can reduce Eq.(12) to the principal axes of the tensor ϵ_{ij} which are also called the principal dielectric axes. In fact, there are some advantages to writing Eq.(12) in the principal dielectric axes. In this case it exactly coincides with Fresnel's equation which is the main equation of crystal optics. In general, Eq.(12) determines the wave-vector surface in the n_x, n_y, n_z coordinates. Such surfaces depend upon three constant coefficients $\epsilon_x, \epsilon_y, \epsilon_z$ (eigenvalues of the dielectric tensor ϵ_{ij}).

For homogeneous solutions the Fresnel's equation simplifies significantly, since is these systems $\epsilon_x = \epsilon_y = \epsilon_z$. We want to consider such a transition in the two following steps. First, consider the case of two different eigenvalues $\epsilon_x = \epsilon_y = \epsilon_\perp$ and $\epsilon_z = \epsilon_\parallel$ (these values of parameters correspond to uniaxial crystals). In this case the Fresnel's equation can be factorized to the form

$$(n^2 - \epsilon_\perp)[\epsilon_\parallel n_z^2 + \epsilon_\perp(n_x^2 + n_y^2) - \epsilon_\perp \epsilon_\parallel] = 0 \qquad (13)$$

where $\mathbf{n} = (n_x, n_y, n_z)$ is the direction of the light propagation. In other words, an equation of the fourth order (upon n) is reduced to the product of the two quadratic equations

$$n^2 = n_x^2 + n_y^2 + n_z^2 = \epsilon_\perp \qquad (14)$$

$$\frac{n_z^2}{\epsilon_\perp} + \frac{n_x^2 + n_y^2}{\epsilon_\parallel} = 1 \qquad (15)$$

where the first equation is the equation of a sphere, while the second equation determines an ellipsoid. The sphere represents the propagation of ordinary waves. Such waves have the same refractive index $n = \sqrt{\epsilon_\perp}$. The second equation represents the so-called extraordinary waves which are directly related with the optical activity. Let us consider the extraordinary waves in homogeneous solutions, or in crystals of a cubic system. These two cases can be obtained as the limit of Eq.(15) when $\epsilon_\parallel \to \epsilon_\perp$. In reality, it can be written in the two different forms $\epsilon_\parallel = \epsilon_\perp \pm \Delta$, where the positive parameter $\Delta \to 0$. In such cases, Eq.(14) does not change, while the second equation takes the form

$$\frac{n_z^2}{\epsilon_\perp} + \frac{n_x^2 + n_y^2}{\epsilon_\perp \pm \Delta} = 1 \quad or \quad \frac{n^2 cos^2\theta}{\epsilon_\perp} + \frac{n^2 sin^2\theta}{\epsilon_\perp \pm \Delta} = 1 \qquad (16)$$

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where $n_x = n \cdot \sin\theta \cos\phi, n_y = n \cdot \sin\theta \sin\phi, n_z = n \cdot \cos\theta$, where θ is the angle between the optical axis and vector $\mathbf{n}$.

In homogeneous solutions the orientation of chiral molecules is random, i.e. we have to replace the factors $cos^2\theta$ and $sin^2\theta$ in the last equation by their mean values $\frac{1}{2}$. This gives

$$\frac{1}{\epsilon_\perp} + \frac{1}{\epsilon_\perp \pm \Delta} = \frac{2}{n^2} \tag{17}$$

or

$$\frac{2}{n^2} = \frac{\epsilon_\perp + \epsilon_\perp \pm \Delta}{\epsilon_\perp(\epsilon_\perp \pm \Delta)} \approx \frac{2(\epsilon_\perp \pm \frac{1}{2}\Delta)}{(\epsilon_\perp \pm \frac{1}{2}\Delta)^2} = \frac{2}{(\epsilon_\perp \pm \frac{1}{2}\Delta)} \tag{18}$$

From here one finds that $n^2 = \epsilon_\perp \pm \frac{1}{2}\Delta$, or in other words, we have two different refractive indices $n_1^2 = \epsilon_\perp + \frac{1}{2}\Delta$ and $n_2^2 = \epsilon_\perp - \frac{1}{2}\Delta$. This means that two different refracted wave are formed and, formally, we have to consider the double refraction or birefringence. However, the parameter Δ is small (in fact, very small) in comparison with n^2. Therefore, the overall scale of such a birefringence is $\approx \Delta$.

Result can be obtained in a slightly different way with the use of some microscopic identities. Indeed, let us note that for homogeneous solutions of chiral molecules $\epsilon_{ij} = \epsilon \cdot \delta_{ik} + i\frac{c}{\omega}f(\omega)e_{ikl}n_l$, where e_{ikl} is the complete antisymmetric tensor. In this case we do not need to use the complete Fresnel's equation to produce the same answer as above. The chiral activity can be described with the use of only one numerical parameter $f(\omega)$ which is pseudoscalar. In fact, such a parameter can be introduced in a slightly different way. Indeed, the Maxwell equations in the case of homogeneous solutions take the form

$$\mathbf{D} = \epsilon\mathbf{E} - g\frac{\partial\mathbf{H}}{\partial t} \quad , \quad \mathbf{B} = \mu\mathbf{H} + g\frac{\partial\mathbf{E}}{\partial t} \tag{19}$$

where g is a some constant, which depends upon ω. By taking into account polarization of media by the electric and magnetic field we can write, e.g., for the $\mathbf{D}$ vector

$$\mathbf{D} = (1 + 4\pi N\alpha)\mathbf{E} - 4\pi N\frac{\beta}{c}\frac{\partial\mathbf{H}}{\partial t} \tag{20}$$

where α is the static polarizability, while β is the so-called optical rotatory parameter, or optical rotation, for short. As follows from Eq.(20) the parameter β is also a pseudoscalar. The parameter β determines the optical rotation, i.e. the rotation of the plane of left- and right-circularly polarized light when it passes through an optically active medium. Also, in this equation N is the number of chiral molecules per unit volume. It follows from the last

two equations that $\epsilon = 1 + 4\pi N\alpha$ and $g = 4\pi N\frac{\beta}{c}$. The relation between factor g and the indices of refraction for circularly polarized light can also be obtained from Eq.(20)

$$\chi_L = \sqrt{\epsilon} - 2\pi\omega g \quad and \quad \chi_R = \sqrt{\epsilon} + 2\pi\omega g \tag{21}$$

Now it is easy to find the overall rotation (δ) when the light propagates the distance z in some chiral media

$$\delta = \frac{\pi z}{\lambda}(\chi_R - \chi_L) = \frac{4\pi^2 z}{\lambda^2}g = 4\pi^2\nu^2 z \cdot g = \frac{16\pi^3\nu^2 Nz}{c} \cdot \beta \tag{22}$$

Note that the optical rotatory parameter β (as well as α) which follows from Eq.(20) can rigorously be determined only with the use of the quantum mechanics of molecules. This will be our goal in the third Section.

III. STOKES PARAMETERS

As follows from its definition any monochromatic wave has a certain polarization. However, in actual optical experiments it is almost impossible to create a beam of pure monochromatic waves, and usually we have to operate with real light which contains frequencies distributed in a small interval $\Delta\omega$ around the main frequency ω. The means that the real light is, in fact, a mixture of light quanta with different polarizations. An arbitrary property of such a beam of light, e.g., the electric field $\mathbf{E}$, in the real light depends upon time. If the frequency distribution $\Delta\omega$ around ω is narrow, then the $\mathbf{E}(t)$ function can be represented in the form $\mathbf{E}(t) = \mathbf{E}_0(t)exp(-\imath\omega t)$, where $\mathbf{E}_0(t)$ is a slowly varying function of time t which determines the polarization of the actual light. From the last formula one can expect that such a polarization will be slowly changing in time, i.e. we are dealing with the partially polarized light [3].

In regular experiments we cannot observe the polarization properties of electromagnetic waves directly. Instead, one measures the intensity distribution of light when it passes through various physical bodies. This means we are dealing with quadratic functions of the field. In other words, in actual experiments we are measuring the components of the following tensor $J_{\alpha\beta} = \overline{E_{0\alpha}E_{0\beta}^*}$, where $E_{0\alpha}$ and $E_{0\beta}^*$ are the Cartesian components of the slow varying $\mathbf{E}_0(t)$ vector. The line over the product of the two complex vectors mean the value averaged in time. If all vectors are represented in the form $\mathbf{E}(t) = \mathbf{E}_0(t)exp(-\imath\omega t)$,

then the $E_{0\alpha}E_{0\beta}^*$ product is the only value which has non-zero time-average. Other similar combinations, i.e., $E_{0\alpha}^*E_{0\beta}^*$ and $E_{0\alpha}E_{0\beta}$, contain rapidly oscillating factors $exp(-2\imath\omega t)$ which gives zero upon time averaging.

Since in any plane wave one finds $\mathbf{E} \perp \mathbf{n}$, where $\mathbf{n}$ is the direction of wave propagation, then the $J_{\alpha\beta}$ tensor has only four components. Moreover, the $J_{\alpha\beta}$ tensor also contains the total intensity of the wave $J = \sum_\alpha J_{\alpha\alpha} = \overline{\mathbf{E} \cdot \mathbf{E}^*}$. This value has nothing to do with with polarization of the wave and can be excluded by introducing the tensor $\rho_{\alpha\beta} = \frac{J_{\alpha\beta}}{J}$. The tensor $\rho_{\alpha\beta}$ has the unit trace and it is called the polarization tensor. It can be shown that the polarization tensor is hermitian, i.e. $\rho_{\alpha\beta}^* = \rho_{\beta\alpha}$. Now, we can introduce the degree of polarization P which is defined as

$$P = \sqrt{1 - 4det(\rho_{\alpha\beta})} = \sqrt{1 - 4\rho_{11}\rho_{22} + 4 \mid \rho_{12} \mid^2} \tag{23}$$

where $det(\rho_{\beta\alpha})$ is the determinant of the 2×2 matrix $\rho_{\beta\alpha}$.

An arbitrary hermitian 2×2 matrix can be represented in the following form

$$\rho_{\alpha\beta} = \frac{1}{2}(\rho_{\alpha\beta} + \rho_{\beta\alpha}) + \frac{1}{2}(\rho_{\alpha\beta} - \rho_{\beta\alpha}) = S_{\alpha\beta} - \frac{\imath}{2}e_{\alpha\beta}A \tag{24}$$

where $S_{\alpha\beta}$ is the real symmetric 2×2 tensor. The analogous non-symmetric 2×2 tensor in two-dimensional space is reduced to the unit antisymmetric tensor $e_{12} = -e_{21}$ and pseudoscalar A. The pseudoscalar A is called the degree of circular polarization. It is bounded between -1 and +1. The case of a light wave with linear polarization corresponds to the $A = 0$ value. The waves with circular polarization correspond to the values $A = +1$ (right-circular) polarization and $A = -1$ (left-circular polarization).

An alternative expansion for an arbitrary hermitian 2×2 matrix is performed with the use of three Pauli matrices $\hat{\sigma}_i$ $(i = x, y, z)$ (see, e.g., [4]) and one unit matrix $\hat{I}$. It is written in the form

$$\rho_{\alpha\beta} = \frac{1}{2}\left(\hat{I} + \xi_1\hat{\sigma}_x + \xi_2\hat{\sigma}_y + \xi_3\hat{\sigma}_z\right) = \frac{1}{2}\begin{pmatrix} 1 + \xi_3 & \xi_1 - \imath\xi_2 \\ \xi_1 + \imath\xi_2 & 1 - \xi_3 \end{pmatrix} \tag{25}$$

The parameters ξ_1, ξ_2 and ξ_3 which appear in this formula are the so-called Stokes parameters. In general, any intensity measurement may be written as a linear combination of these three parameters and one additional Stokes parameter ξ_0 which is the total intensity of the scattered light. The determinant of the $\rho_{\beta\alpha}$ tensor is

$$det(\rho_{\alpha\beta}) = \frac{1}{4}(1 - \xi_1^2 - \xi_2^2 - \xi_3^2) \tag{26}$$

while the degree of polarization is $P = \sqrt{\xi_1^2 + \xi_2^2 + \xi_3^2}$. The Stokes parameters ξ_1 and ξ_3 determine the degree of the linear polarization, while the parameter ξ_2 shows the degree of circular polarization. Note that the parameter ξ_2 coincides with the pseudoscalar A introduced above. From three Stokes parameters one can construct the two scalars (ξ_2 and $\sqrt{\xi_1^2 + \xi_3^2}$) which are invariants under Lorentz transformations. The three Stokes parameters also have a number of other advantages in actual applications.

IV. CIRCULAR DICHROISM

In all formulas above we have neglected the absorption of light during its propagation in the dense media. In actual cases the absorption of light always occurs. At some frequencies, e.g., in the vacuum ultraviolet region, it plays a very important role and cannot be ignored even in the first approximation. In reality the situation is even more complicated, since light waves with different circular polarization are absorbed differently by the media. This is called circular dichroism (CD). Such a differential absorption of light with left- and right-circular polarizations can directly (and substantially) affect the observed optical activity. It appears that optical rotation and differential absorption of light with different circular polarizations can be considered as the two manifestations of one phenomenon.

In general, a detailed study of circular dichroism at different frequencies allows one to develop a new approach for analysis of organic substances. In this Section we want to discuss the modification which is required in all formulas presented above. The absorption of light is described by introducing an imaginary part into the permittivity tensor $\epsilon_{ij}(\omega, \mathbf{r})$, or in other words, by considering static polarizability α as a complex value. However, we are not interested here in the total light absorption. Our interest is related to a very specific difference between absorption of light with left- and right-circular polarizations. It is clear that a complex static polarizability α, Eq.(20), cannot describe such differences. As follows from Eq.(20) this goal can be achieved by considering the optical rotatory parameter β as a complex value.

In these cases the parameter β is represented as the sum of its real and imaginary parts, i.e. $\beta = \beta_1 + \imath \beta_2$, where β_1 and β_2 are two functions of the frequency ω. These two functions, however, are not completely independent, since there are two additional connections between them which follow from the Kramers-Kronig relations. This follows from the fact that $\beta(\omega)$

is the response function [2], [6] which is an analytical function in the upper half ω plane (for now, we consider the frequency ω as a complex variable) (see, e.g., [6]). This allows us to use Cauchy's theorem for $\beta(\omega)$:

$$\beta(z) = \frac{1}{2\pi\imath} \oint_C \frac{\beta(\omega')d\omega'}{\omega' - z} \tag{27}$$

The contour C can be chosen to consist of the real frequency axis ω and a great semicircle at infinity in the upper half plane. The function $\beta(\omega)$ vanishes rapidly at infinity, i.e. there is no contribution to the integral from the great semicircle. Finally, Cauchy's integral is written in the form

$$\beta(z) = \frac{1}{2\pi\imath} \int_{-\infty}^{+\infty} \frac{\beta(\omega')d\omega'}{\omega' - z} \tag{28}$$

where z now is any point in the upper $\omega-$half plane and the integral is taken over the real axis. In fact, we want to place the point z at the real axis. This can be done by approaching the real axis from above, i.e. by representing the complex variable z in the form $z = \omega + \imath\varepsilon$. This gives

$$\beta(\omega) = \frac{1}{2\pi\imath} \int_{-\infty}^{+\infty} \frac{\beta(\omega')d\omega'}{\omega' - \omega - \imath\varepsilon} \tag{29}$$

The denominator in the last formula can be written in the form [6]

$$\frac{1}{\omega' - \omega - \imath\varepsilon} = P\Big(\frac{1}{\omega' - \omega}\Big) + \pi\imath\delta(\omega' - \omega) \tag{30}$$

where the symbol P means the principal part, while $\delta(x)$ designates the Dirac delta-function. Now Eq.(29) takes the form

$$\beta(\omega) = \frac{1}{\pi\imath} P \int_{-\infty}^{+\infty} \frac{\beta(\omega')d\omega'}{\omega' - \omega} \tag{31}$$

By separating here the real and imaginary parts one finds

$$Re\beta(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{Im\beta(\omega')d\omega'}{\omega' - \omega} \tag{32}$$
$$Im\beta(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{Re\beta(\omega')d\omega'}{\omega' - \omega}$$

This is the most general Kramers-Kronig relations written for the optical rotatory parameter β. In general, it can be shown that the $Re\beta(\omega)$ is an even function in ω, while $Im\beta(\omega)$ is odd. This allows one to transform the last two integrals in Eq.(32) to the integrals taken over positive frequencies only, i.e.

$$Re\beta(\omega) = \frac{2}{\pi} P \int_0^{+\infty} \frac{\omega'[Im\beta(\omega')]d\omega'}{(\omega')^2 - \omega^2} \tag{33}$$
$$Im\beta(\omega) = -\frac{2\omega}{\pi} P \int_0^{+\infty} \frac{[Re\beta(\omega')]d\omega'}{(\omega')^2 - \omega^2}$$

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These formulas can be used in actual applications which include the optical rotatory parameter β. By using Eq.(22) we can re-write these formulas for the corresponding angles $\delta = \theta + \imath\kappa$

$$\theta(\nu) = \frac{2}{\pi} P \int_0^{+\infty} \frac{\nu'\kappa(\nu')d\nu'}{(\nu')^2 - \nu^2}$$

$$\kappa(\nu) = -\frac{2\nu}{\pi} P \int_0^{+\infty} \frac{\theta(\nu')d\nu'}{(\nu')^2 - \nu^2}$$

(34)

where we have also introduced the linear frequency $\nu = \frac{\omega}{2\pi}$ (ω is called the circular frequency). The importance of the linear frequencies ν follows from the fact that these values are usually used in actual experiments. In general, Eq.(34) represents the explicit relation between the actual optical rotation (angle θ) and circular dichroism (angle κ). As follows from Eq.(34) the optical rotation known for all frequencies allows one to determine the circular dichroism at each frequency [5]. In reality, however, one finds a number of restrictions which exist in the solution of this problem. Most of such restrictions follow from the fact that optical rotations in the VUV region ($\lambda \leq 150 \ nm$) are not known even approximately. On the other hand, it is clear that for each molecule the VUV area of wavelengths contains many resonance lines which are crucially important to describe the absorbtion of radiation. If we ignore the VUV region of wavelengths, then we can restore the circular dichroism at all frequencies only approximately (in reality, very approximately). For some limited areas of wavelengths, however, such a reconstruction can be quite accurate and complete. Usually, these areas of wavelengths are located far from the VUV region.

Note also, that the experimental knowledge of the $\theta(\nu)$ and $\kappa(\nu)$ values for large number of different frequencies $\nu_1, \nu_2, \ldots, \nu_n$ is used to detect uniformly the corresponding organic substance. Formally, such an identification allows one to solve many problems of quantative and qualitative analysis of the mixtures of chiral organic substances.

V.   TENSOR OF MOLECULAR OPTICAL ACTIVITY. ROTATION POWER.

In the middle of 1930's Placzek shown [7] that a significant number of effects related to the interaction between atom(s) and electromagnetic field can be described with the use of only one tensor, later known as the tensor of light scattering. In particular, the differential scattering cross-section of light by an atom (or any other electron containing system) can

be written in the form

$$d\sigma = \frac{\omega(\omega + \omega_{12})^3}{\hbar^2 c^4} \mid (C_{ik})_{21}(\mathbf{e}'_i)^* \mathbf{e}_k \mid^2 do' \tag{35}$$

where $(C_{ik})_{21}$ is the 3×3 tensor of light scattering, while $\mathbf{e}_i$ and $\mathbf{e}_k$ are the polarization vectors of the incident and final photons. The integration in Eq.(35) is performed over the angular variables of the final photon which is designated by the superscript $'$. Here and everywhere below we shall assume that the angular volume element do' has the form $do' = sin\theta' d\theta' d\phi$. The explicit expression for the light scattering tensor $(C_{ik})_{21}$ is [8]

$$(C_{ik})_{21} = \sum_n \Big[\frac{(d_i)_{2n}(d_k)_{n1}}{\omega_{n1} - \omega - \imath 0} + \frac{(d_k)_{2n}(d_i)_{n1}}{\omega_{n1} + \omega' - \imath 0} \Big] \tag{36}$$

where $\omega' = \omega + \omega_{12}$, while d_i and d_k are the corresponding components of the vector of the dipole moment $\mathbf{d}$. Note that the differential cross-section $d\sigma$, Eq.(35), corresponds to the lowest order approximation upon the fine structure constant $\alpha \approx \frac{1}{137}$ and contains only the electric dipole-dipole interaction.

The Placzek approach for atoms suggests attempting to derive an analogous method for molecules which would describe their optical activity. In this Section this problem is considered in detail and it is shown that in the lowest order approximation can be described by the tensor $(C_{ik})_{21}$ of light scattering and by the four (or two in some cases) new tensors. These tensors are called the tensors of (molecular) optical activity. Note that in many actual cases the four/two tensors of optical activity are reduced to one tensor only. To produce the closed analytical expressions for these tensors below we shall assume that the electromagnetic field is represented as a combination of plane waves. Each of these plane waves has its own frequency ω and polarization which is represented by the vector $\mathbf{e}$. The wave functions of the incident and final photons can be taken in the form (see, e.g., [8])

$$\mathbf{A}_{\mathbf{e}\omega} = \sqrt{\frac{2\pi}{\omega}} exp(-\imath\omega t + \imath\mathbf{k} \cdot \mathbf{r})\mathbf{e} \quad , \quad \mathbf{A}_{\mathbf{e}'\omega'} = \sqrt{\frac{2\pi}{\omega'}} exp(-\imath\omega' t + \imath\mathbf{k}' \cdot \mathbf{r}')\mathbf{e}' \quad , \tag{37}$$

where ω and ω' are the corresponding frequencies, while vectors $\mathbf{e}$ and $\mathbf{e}'$ represent the polarization of the incident and final photons, respectively. Below, we shall consider the plane waves in the transverse (or radiation) gauge, where $div\mathbf{A} = 0$. In this gauge one finds $\mathbf{k} \cdot \mathbf{e} = 0$ and $\mathbf{k}' \cdot \mathbf{e}' = 0$. Note that in calculations for the final photon we need to use the wave function which is conjugate to its wave function, i.e. $\mathbf{A}^*_{\mathbf{e}'\omega'}$. As follows from these

equations the electric $\mathbf{E}$ and magnetic $\mathbf{H}$ fields are

$$\mathbf{E_{e\omega}} = -\frac{\partial}{\partial t}\mathbf{A_{e\omega}} = -\imath\sqrt{2\pi\omega}\mathbf{e}exp(-\imath\omega t + \imath\mathbf{k}\cdot\mathbf{r}) \tag{38}$$

$$\mathbf{H_{e\omega}} = curl\mathbf{A_{e\omega}} = \imath\sqrt{\frac{2\pi}{\omega}}(\mathbf{k}\times\mathbf{e})exp(-\imath\omega t + \imath\mathbf{k}\cdot\mathbf{r})$$

By introducing the unit vector $\mathbf{n} = \frac{\mathbf{k}}{\omega}$ we can re-write the last equation in the form

$$\mathbf{H_{e\omega}} = \imath\sqrt{2\pi\omega}(\mathbf{n}\times\mathbf{e})exp(-\imath\omega t + \imath\mathbf{k}\cdot\mathbf{r}) \tag{39}$$

Analogous expressions can be obtained for the $\mathbf{E_{e'\omega'}}$ and $\mathbf{H_{e'\omega'}}$ fields which are related with the $\mathbf{A_{e'\omega'}^{*}}$ wave function.

From these equations one finds the following expressions for the electric dipole and magnetic dipole interactions. In fact, for each of the $(\mathbf{e},\omega)$-components of the $\mathbf{E}$ and $\mathbf{H}$ vectors we have

$$V_{\mathbf{e\omega}}^{e} = -\mathbf{d}\cdot\mathbf{E_{e\omega}} = \imath\sqrt{2\pi\omega}(\mathbf{d}\cdot\mathbf{e})exp(-\imath\omega t + \imath\mathbf{k}\cdot\mathbf{r}) \tag{40}$$

and

$$V_{\mathbf{e\omega}}^{m} = -\mathbf{m}\cdot\mathbf{H_{e\omega}} = -\imath\sqrt{2\pi\omega}[\mathbf{m}\cdot(\mathbf{n}\times\mathbf{e})]exp(-\imath\omega t + \imath\mathbf{k}\cdot\mathbf{r}) \tag{41}$$

where $\mathbf{d}$ and $\mathbf{m}$ are the vectors of the electric and magnetic dipole moments, respectively. In the lowest order approximation the one-photon matrix elements of the V^{e} and V^{m} interactions equal zero identically. The first non-zero contribution can be found only in the second order of perturbation theory. In the second order approximation the matrix element V_{21} for the transition between states 1 and 2 is written in the following form [8]

$$V_{21} = \sum_{n}\Big(\frac{V_{2n}'V_{n1}}{\mathcal{E}_1 - \mathcal{E}_n^I} + \frac{V_{2n}V_{n1}'}{\mathcal{E}_1 - \mathcal{E}_n^{II}}\Big) \tag{42}$$

where the notation $\mathcal{E}$ designates the total energy of the system ('molecule + photons'), i.e. in the case considered here we have $\mathcal{E}_n^I = E_n$ and $\mathcal{E}_n^{II} = E_n + \omega + \omega'$. The matrix elements V_{ab} represent absorbtion of the photon with the wave vector $\mathbf{k}$. Analogously, the matrix elements V_{ab}' represent emission of the photon with the wave vector $\mathbf{k}'$. In the general case, in Eq.(42) the $V = V_{21}$ interaction is represented in the form $V = V^e + V^m + V^{qe} + V^{qm} + \ldots$ and $V' = (V^e)' + (V^m)' + (V^{qe})' + (V^{qm})' + \ldots$, where V^e, V^m, V^{qe} are the electric dipole, magnetic dipole and electric quadruple interactions, respectively. Keeping only lowest order terms in the expansion of V in terms of the fine-structure constant $\alpha \approx \frac{1}{137}$, we can write

$V \approx V^e + V^m$ and $V' \approx (V^e)' + (V^m)'$. In this case one finds from Eq.(42)

$$V_{21} = \sum_n \Big[\frac{(V^e)'_{2n}V^e_{n1}}{\mathcal{E}_1 - \mathcal{E}^I_n} + \frac{(V^e)_{2n}(V^e)'_{n1}}{\mathcal{E}_1 - \mathcal{E}^{II}_n}\Big] + \sum_n \Big[\frac{(V^e)'_{2n}V^m_{n1}}{\mathcal{E}_1 - \mathcal{E}^I_n} + \frac{(V^e)_{2n}(V^m)'_{n1}}{\mathcal{E}_1 - \mathcal{E}^{II}_n} + \frac{(V^m)'_{2n}V^e_{n1}}{\mathcal{E}_1 - \mathcal{E}^I_n} \quad (43)$$

$$+ \frac{(V^m)_{2n}(V^e)'_{n1}}{\mathcal{E}_1 - \mathcal{E}^{II}_n}\Big] + \sum_n \Big[\frac{(V^m)'_{2n}V^m_{n1}}{\mathcal{E}_1 - \mathcal{E}^I_n} + \frac{(V^m)_{2n}(V^m)'_{n1}}{\mathcal{E}_1 - \mathcal{E}^{II}_n}\Big] + \cdots$$

By neglecting here by all terms $\sim V^m V^m$ and other terms of higher orders in the fine structure constant α, we obtain the following formula for the differential cross-section of light scattering $d\sigma$

$$d\sigma = \mid V_{21} \mid^2 \frac{(\omega')^2 do'}{4\pi^2} = d\sigma_{ee} + d\sigma_{em} \tag{44}$$

where $d\sigma_{ee}$ is the part of the total cross-section which can be reduced to the expression given above (see Eq.(35)). This part of the cross-section is not related with the optical activity. The second term in the right-hand side of Eq.(44) is significantly smaller, in the general case, than the first term, i.e. $d\sigma_{em} \ll d\sigma_{ee}$. However, the second term in Eq.(44) is a great interest, since it represents all lowest order effects which are determined by the molecular optical activity.

As follows from Eq.(43) in order to determine the part of the total cross-section responsible for molecular optical activity in the lowest order approximation we need to obtain the explicit formulas for the matrix elements of the $V^e V^e, V^e V^m$, and $V^m V^e$ products. The arising expressions are extremely complicated, since each of the V^e and/or V^m interactions contains an infinite number of $V^e_{\mathbf{e}\omega}$ and $V^m_{\mathbf{e}\omega}$ components. In the $V^e V^m$ and/or $V^m V^e$ products one finds an infinite number of cross-terms which explicitly depend upon coordinates. These terms cannot be computed without a complete and accurate knowledge of the molecular electron density $\rho_e(\mathbf{r})$.

However, we can introduce an approximation that the wavelengths λ of the incident and final photons are significantly larger than typical linear sizes of molecule a (our light scatterer). In this case we have $\mathbf{k} \cdot \mathbf{r} \leq \mid \mathbf{k} \mid\mid \mathbf{r} \mid \ll \frac{a}{\lambda} \approx 0$. In this approximation one finds from Eqs.(40) and (41)

$$\mathbf{E}_{\mathbf{e}\omega} = -\imath\sqrt{2\pi\omega}\mathbf{e}exp(-\imath\omega t) \tag{45}$$

and

$$\mathbf{H}_{\mathbf{e}\omega} = \imath\sqrt{2\pi\omega}(\mathbf{n} \times \mathbf{e})exp(-\imath\omega t) \quad . \tag{46}$$

Therefore, we can write

$$V^e_{\mathbf{e}\omega} = \imath\sqrt{2\pi\omega}(\mathbf{d} \cdot \mathbf{e})exp(-\imath\omega t) = \imath\sqrt{2\pi\omega}(\mathbf{d}_\omega \cdot \mathbf{e}) \tag{47}$$

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and

$$V_{\mathbf{e}\omega}^m = -\imath\sqrt{2\pi\omega}[\mathbf{m}\cdot(\mathbf{n}\times\mathbf{e})]exp(-\imath\omega t) = -\imath\sqrt{2\pi\omega}[\mathbf{m}_\omega\cdot(\mathbf{n}\times\mathbf{e})] \qquad (48)$$

where $\mathbf{d}_\omega$ and $\mathbf{m}_\omega$ are the corresponding Fourier-components of the dipole and magnetic moments of the molecule. Note that with the identity $\mathbf{m}\cdot(\mathbf{n}\times\mathbf{e}) = \mathbf{e}\cdot(\mathbf{m}\times\mathbf{n})$, the formula for magnetic interaction can also be written in another form

$$V_{\mathbf{e}\omega}^m = -\imath\sqrt{2\pi\omega}[(\mathbf{m}_\omega\times\mathbf{n})\cdot\mathbf{e}] \qquad (49)$$

which is similar to the formula for $V_{\mathbf{e}\omega}^e$ in which the vector of the dipole momentum $\mathbf{d}$ is replaced by the vector-product $\mathbf{m}_\omega\times\mathbf{n}$.

Now, we can write the lowest order term upon the magnetic interaction in the differential cross-section $d\sigma$ of the light scattering

$$d\sigma = \Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')(\mathbf{d}_{n1}\cdot\mathbf{e})}{\omega_{n1}-\omega-\imath 0} + \frac{(\mathbf{d}_{2n}\cdot\mathbf{e})(\mathbf{d}_{n1}\cdot\mathbf{e}')}{\omega_{n1}+\omega'-\imath 0}\Big|\Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')[(\mathbf{m}_{n1}\times\mathbf{n})\cdot\mathbf{e}]}{\omega_{n1}-\omega-\imath 0} + (50)$$

$$\frac{[(\mathbf{m}_{2n}^*\times\mathbf{n})\cdot\mathbf{e}'](\mathbf{d}_{n1}\cdot\mathbf{e})}{\omega_{n1}-\omega-\imath 0} + \frac{(\mathbf{d}_{2n}\cdot\mathbf{e})[(\mathbf{m}_{n1}^*\times\mathbf{n})\cdot\mathbf{e}']}{\omega_{n1}+\omega'-\imath 0} + \frac{[(\mathbf{m}_{2n}\times\mathbf{n})\cdot\mathbf{e}](\mathbf{d}_{n1}\cdot\mathbf{e}')}{\omega_{n1}+\omega'-\imath 0}\Big|\cdot\frac{\omega(\omega')^3}{\hbar^2 c^4}do'$$

where the notation $\mathbf{e}'$ designates the vector $(\mathbf{e}')^*$. This notation is also used in the two following equations. This equation can be re-written as

$$d\sigma = \Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')(\mathbf{d}_{n1}\cdot\mathbf{e})}{\omega_{n1}-\omega-\imath 0} + \frac{(\mathbf{d}_{2n}\cdot\mathbf{e})(\mathbf{d}_{n1}\cdot\mathbf{e}')}{\omega_{n1}+\omega'-\imath 0}\Big|\Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')[\mathbf{m}_{n1}\cdot(\mathbf{n}\times\mathbf{e})]}{\omega_{n1}-\omega-\imath 0} + (51)$$

$$\frac{[\mathbf{m}_{2n}^*\cdot(\mathbf{n}\times\mathbf{e}')](\mathbf{d}_{n1}\cdot\mathbf{e})}{\omega_{n1}-\omega-\imath 0} + \frac{(\mathbf{d}_{2n}\cdot\mathbf{e})[\mathbf{m}_{n1}^*\cdot(\mathbf{n}\times\mathbf{e}')]}{\omega_{n1}+\omega'-\imath 0} + \frac{[\mathbf{m}_{2n}\cdot(\mathbf{n}\times\mathbf{e})](\mathbf{d}_{n1}\cdot\mathbf{e}')}{\omega_{n1}+\omega'-\imath 0}\Big|\cdot\frac{\omega(\omega')^3}{\hbar^2 c^4}do'$$

In these equations and below the notation $\mathbf{m}^*$ stands for the vector which is a complex conjugate vector to the vector of magnetic dipole moment $\mathbf{m}$. In quantum mechanics (in the coordinate representation) we always have $\mathbf{d}^* = \mathbf{d}$, but $\mathbf{m}^* \neq \mathbf{m}$. Note that the vector $\mathbf{n}$ in these equations corresponds to the direction of the scattered light. Formally, this vector can be oriented in an arbitrary spatial direction, but in almost all modern experiments on optical activity in homogeneous solutions the direction of the scattered light always coincides with the direction of the incident light. This means that our differential cross-section must be multiplied by a delta-function $\delta(\mathbf{n}_{in}-\mathbf{n})$ and integrated over the angular variables $o' = (\theta',\phi')$ of the unit vector $\mathbf{n} = (cos\theta' cos\phi', cos\theta' sin\phi', sin\theta')$ which represents the direction of the final photon. The unit vector $\mathbf{n}_{in}$ describes the direction of the incident photon. This produces the following expression for the cross-section σ

$$\sigma = \frac{4\pi\omega(\omega+\omega_{12})^3}{\hbar^2 c^4}\cdot\Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')(\mathbf{d}_{n1}\cdot\mathbf{e})}{\omega_{n1}-\omega-\imath 0} + \frac{(\mathbf{d}_{2n}\cdot\mathbf{e})(\mathbf{d}_{n1}\cdot\mathbf{e}')}{\omega_{n1}+\omega'-\imath 0}\Big|\Big|\sum_n\frac{(\mathbf{d}_{2n}\cdot\mathbf{e}')[\mathbf{m}_{n1}\cdot(\mathbf{n}_{in}\times\mathbf{e})]}{\omega_{n1}-\omega-\imath 0}$$

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$$+\frac{[\mathbf{m}_{2n}^* \cdot (\mathbf{n}_{in} \times \mathbf{e}')](\mathbf{d}_{n1} \cdot \mathbf{e})}{\omega_{n1} - \omega - \imath 0} + \frac{(\mathbf{d}_{2n} \cdot \mathbf{e})[\mathbf{m}_{n1}^* \cdot (\mathbf{n}_{in} \times \mathbf{e}')]}{\omega_{n1} + \omega' - \imath 0} + \frac{[\mathbf{m}_{2n} \cdot (\mathbf{n}_{in} \times \mathbf{e})](\mathbf{d}_{n1} \cdot \mathbf{e}')}{\omega_{n1} + \omega' - \imath 0} \quad (52)$$

where $\omega' = \omega + \omega_{12}$ and unit-vector $\mathbf{n}_{in}$ designates the direction of propagation of the incident photon.

The expression, Eq.(52), can be cast in the following form

$$\sigma = \frac{4\pi\omega(\omega + \omega_{12})^3}{\hbar^2 c^4} \cdot \left|(C_{ik})_{21}(\mathbf{e}'_i)^* \mathbf{e}_k\right| \cdot \left|(\hat{S}_{ik})_{21}(\mathbf{e}')_i^* (\mathbf{n}_{in} \times \mathbf{e})_k + (\hat{T}_{ik})_{21}(\mathbf{n}_{in} \times (\mathbf{e}')^*)_i \mathbf{e}_k \right. \quad (53)$$

$$\left. + (\hat{U}_{ik})_{21}(\mathbf{e})_i(\mathbf{n}_{in} \times (\mathbf{e}')^*)_k + (\hat{V}_{ik})_{21}(\mathbf{n}_{in} \times \mathbf{e}')_i(\mathbf{e}'_k)^*\right|$$

where $(S_{ik})_{21}, (T_{ik})_{21}, (U_{ik})_{21}$ and $(V_{ik})_{21}$ are 3×3 tensors, while the dipole-dipole tensor $(C_{ik})_{21}$ is defined above in Eq.(36). Here we assume that, in the general case, the vectors $\mathbf{e}'$ and $\mathbf{e}$ which represent the polarization of light are complex. Each of these tensors is represented as a sum of its irreducible components, e.g., $S_{ik} = S^0\delta_{ik} + S_{ik}^s + S_{ik}^a$, where

$$S^0 = \frac{1}{3}S_{ii} \quad , \quad S_{ik}^s = \frac{1}{2}(S_{ik} + S_{ki}) - S^0\delta_{ik} \quad , \quad S_{ik}^a = \frac{1}{2}(S_{ik} - S_{ki}) \quad (54)$$

Note also that S^0, T^0, U^0 and V^0 are called the scalar parts of the S, T, U and V tensors, respectively. The components with the superscripts s and/or a (e.g., T^s, T^a) are the symmetric and antisymmetric parts of the tensor. All components of the $S^0, T^0, U^0, V^0, S_{ik}^s, T_{ik}^s, U_{ik}^s, V_{ik}^s, S_{ik}^a, T_{ik}^a, U_{ik}^a$ and V_{ik}^a tensors contain the products of the corresponding components of the $\mathbf{d}$ and $\mathbf{m}$ vectors, which are the vectors of the electric dipole momentum and magnetic dipole momentum, respectively. The vector-operators which represent the electric and magnetic dipole momenta are assumed to be self-conjugate. Furthermore, as mentioned above in the coordinate representation the vector $\mathbf{d}$ is a real vector (i.e. $\mathbf{d}^* = \mathbf{d}$), while the vector $\mathbf{m}$ is a complex vector (i.e. $\mathbf{m}^* \neq \mathbf{m}$). For instance, the explicit expressions for the S^0, T^0, U^0 and V^0 tensors (they are called the scalar-components) are

$$(S^0)_{21} = \frac{1}{3}\sum_n \frac{(d_i)_{2n}(m_i)_{n1}}{\omega_{n1} - \omega} \quad , \quad (T^0)_{21} = \frac{1}{3}\sum_n \frac{(m_i^*)_{2n}(d_i)_{n1}}{\omega_{n1} - \omega} \quad , \quad (55)$$

$$(U^0)_{21} = \frac{1}{3}\sum_n \frac{(d_i)_{2n}(m_i^*)_{n1}}{\omega_{n2} + \omega} \quad , \quad (V^0)_{21} = \frac{1}{3}\sum_n \frac{(m_i)_{2n}(d_i)_{n1}}{\omega_{n2} + \omega} \quad ,$$

respectively. Analogous formulas for the symmetric and antisymmetric parts of the S, T, U and V tensors are significantly more complicated. These formulas and the physical meaning of all irreducible components of these S, T, U and V tensors will be discussed elsewhere.

Thus, we have shown that all phenomena related to the optical activity can completely be described with the use of only four tensors: $\hat{S}_{21}, \hat{T}_{21}, \hat{U}_{21}$ and $\hat{V}_{21}$. The fifth tensor $\hat{C}_{21}$ (the tensor of electric-dipole light scattering) is included in the formula for the

cross-section as an amplification factor. These five tensors have fifteen irreducible tensor-components $C^0, C_{ik}^s, C_{ik}^a, S^0, T^0, U^0, V^0, S_{ik}^s, T_{ik}^s, U_{ik}^s, V_{ik}^s, S_{ik}^a, T_{ik}^a, U_{ik}^a$ and V_{ik}^a. The first three tensors C^0, C_{ik}^s, C_{ik}^a here have nothing to do with the optical activity itself. Instead they determine the amplification factor which also appears to be $\omega-$dependent. The optical activity is described by the twelve tensors $(S^0, T^0, U^0, V^0, S_{ik}^s, T_{ik}^s, U_{ik}^s, V_{ik}^s, S_{ik}^a, T_{ik}^a, U_{ik}^a$ and $V_{ik}^a)$. In many real applications, however, the total number of independent tensors can be reduced. For instance, if the 1- and 2-states are identical and $\omega_{21} = 0$ (Rayleigh scattering), then to describe optical activity one needs only two tensors (not four!) with six irreducible components. This case corresponds to the regular optical activity (optical rotation) measured in modern experiments with dilute solutions of organic molecules. Furthermore, if the polarization vectors are always chosen as real (not complex), then to describe the optical activity one needs only one 3×3 tensor with three irreducible components. However, the explicit $\omega-$dependence of such a tensor will be quite complicated. All such cases will be considered in our next study.

The intensity of the scattered light I' is uniformly related to the intensity of the incident light I by the relation

$$I' = \left(\frac{\omega'}{\omega}\right)\sigma I \qquad (56)$$

As follows from the formula for the cross-section σ, Eq.(52), in any optically active solution the intensity of the (scattered) light will always be rotated during its propagation along the direction $\mathbf{n}_{in}$. The factor $\left(\frac{\omega'}{\omega}\right)\sigma$ in the last formula can be considered as the rotation power. As follows from the last formula the uniform combination of the twelve tensors mentioned above multiplied by the amplification factor, Eq.(36), allows one to determine the so-called rotation power of the given optically active solution for the initially polarized light. Note that only our approach produces the correct and complete formula for the $\omega-$dependence of the rotation power.

VI. QUANTUM THEORY OF MOLECULAR OPTICAL ACTIVITY

As can be seen above, the physical origin of the relations between different parameters used in classical theory of optical activity remains unknown. The corresponding analytical expressions, numerical values and all possible relations between such 'phenomenological' parameters can be found only with the use of modern quantum theory based on Quantum

Electrodynamics. The first and very important step in the development of quantum origin of optical activity was made by Rosenfeld almost 80 years ago [1]. Below, we shall follow the same general direction. Our main goal in this Section is to obtain the relation between the optical rotatory parameter β from Eq.(22) and properties of an isolated molecule. For an isolated molecule the optical rotatory parameter β can only be a function of the molecular 2^ℓ-pole moments. In reality, however, only a few moments with small ℓ ($\ell = 1, 2$) contribute noticeably. As we mentioned above the parameter β is a pseudoscalar. Therefore, the first (largest) term in the expansion of β in terms of 2^ℓ-pole molecular moments is proportional to the scalar product of the dipole vector and the pseudovector of the magnetic moment $\mathbf{d} \cdot \mathbf{m}$. The second term must be proportional to the product $\mathbf{d} \cdot \hat{Q} \cdot \mathbf{m}$, where $\hat{Q}$ is the second order tensor of the electric quadropole momentum.

Below, we shall assume that all molecular wave functions (for the ground and excited states) are known (or can be determined) to very good accuracy. In this case, by using Rosenfeld's formula one can calculate the optical rotatory parameter β (in some studies it is also called the chiral response parameter)

$$\beta = \frac{c}{6\pi\hbar} \sum_b \frac{Im\Big[\langle a \mid \mathbf{d} \mid b\rangle\langle b \mid \mathbf{m} \mid a\rangle\Big]}{\nu_{ab}^2 - \nu^2} \tag{57}$$

where the summation is taken over all intermediate states. In this equation we use the linear frequencies ν instead of circular frequencies ω, where $\omega = 2\pi\nu$. The notation Im designates the imaginary part of the terms written in brackets. Symbols a and b stand for the quantum (molecular) states, while $\mid a\rangle$ and $\mid b\rangle$ mean the corresponding wave functions. Rosenfeld's formula is based on an assumption that all molecular states (ground and excited) have zero widths. In other words, these states are stable, i.e. the decay time is infinite. In general, this is not a very realistic assumption and we need to introduce finite line widths, e.g., $\gamma_{ab}(\nu) = \frac{4\pi^2 e^2 |\mathbf{D}_{ab}|^2 (\nu_a - \nu_b)^3}{3\epsilon_0 \hbar c^3}$ (in SI-units and in the lowest order dipole approximation [9]). The Rosenfeld formula for the optical rotation δ can now be written in the form

$$\delta = \frac{16\pi^2 Nz}{3hc} \sum_b \frac{\nu^2 R_{ab}}{\nu_{ab}^2 - \nu^2 + \imath\nu\gamma_{ab}} \tag{58}$$

where $R_{ab} = Im\Big[\langle a \mid \mathbf{d} \mid b\rangle\langle b \mid \mathbf{m} \mid a\rangle\Big]$ is the so-called rotating power. By separating the real and imaginary parts of this expression one finds for the actual optical rotation

$$\theta = \frac{16\pi^2 Nz}{3hc} \sum_b \frac{\nu^2(\nu_{ab}^2 - \nu^2)R_{ab}}{(\nu_{ab}^2 - \nu^2)^2 + \nu^2\gamma_{ab}^2} \tag{59}$$

and for the circular dichroism

$$\kappa = -\frac{16\pi^2 Nz}{3hc} \sum_b \frac{\nu^3 \gamma_{ab} R_{ab}}{(\nu_{ab}^2 - \nu^2)^2 + \nu^2 \gamma_{ab}^2} \tag{60}$$

where the notations from formula Eq.(34) are used. The definition of rotating power given above corresponds to the dipole-dipole approximation. In the higher order approximation the rotating power must be taken in the form $R_{ab} = Im\left[\langle a \mid \mathbf{d} \mid b\rangle\langle b \mid \mathbf{m} \mid a\rangle + \sum_{cd}\langle a \mid \mathbf{d} \mid c\rangle\langle c \mid \hat{Q} \mid d\rangle\langle d \mid \mathbf{m} \mid a\rangle\right]$. In reality it is very difficult to calculate the matrix elements R_{ab} accurately. However, a number of useful approximate formulas have been derived from the expressions Eq.(59) and Eq.(60). For instance, if in some experiment we can see N peaks in the $\theta(\lambda)$ function and K peaks in the $\kappa(\lambda)$ function, then it is possible to approximate our experimental data by using the two following formulas

$$\theta(\lambda) = \sum_{i=1}^{N} \frac{A_i(\lambda^2 - \lambda_i^2)}{(\lambda^2 - \lambda_i^2)^2 + B_i} \quad and \quad \kappa(\lambda) = \sum_{j=1}^{K} \frac{C_j \lambda}{(\lambda^2 - \lambda_j^2)^2 + D_j} \tag{61}$$

where all numerical parameters A_i, B_i, C_i and D_i must be determined by using the experimental values of θ and κ at different wavelengths $\lambda = \frac{1}{\nu}$. Numerical examples can be found in the book by Djerassi [5].

Rosenfeld's theory of optical activity allows one to determine the relations between basic molecular properties and actual optical rotation and circular dichroism observed in experiments. Indeed, by applying the known molecular wave functions one can compute the values of $\langle a \mid \mathbf{d} \mid b\rangle$ and $\langle b \mid \mathbf{m} \mid a\rangle$ which are used in formulas for θ and κ above. By using these values we can evaluate the rotating powers R_{ab}. Then we can try to approximate the curves $\theta(\nu)$ and $\kappa(\nu)$ obtained in actual experiments. During this step all line widths γ_{ab} can be varied as numerical parameters. In practice, this approach works approximately only for some simple molecules. For many molecules of interest, e.g., for complex molecules used in cancer research, the current accuracy of the numerical determination of the $\langle b \mid \mathbf{m} \mid a\rangle$ values is not sufficient to make accurate comparisons with experiments. In particular, the signs of the $\langle b \mid \mathbf{m} \mid a\rangle$ values can be wrong in a number of cases. In addition to this, Rosenfeld's theory of optical activity is essentially a semi-classical theory, since all radiation fields in this theory are considered classically. The most rigorous analysis of molecular optical activity can be performed only on a basis of modern quantum electrodynamics (QED) [8]. This will be one of our goals in future studies.

VII. SPECIFIC ROTATION BY CHIRAL ORGANIC MOLECULES

In previous Sections we have briefly considered some theoretical aspects of the molecular optical activity at arbitrary wavelengths. In this Section we discuss a few basic features which are known for optically active organic molecules in solutions. In general, if some organic molecule has non-zero electric and magnetic moments, then its optical rotation θ, Eq.(59), differs from zero. Such a molecule shows a number of phenomena which are usually designated as 'optical activity', or briefly, as an optical rotation of plane-polarized light. In principle, any molecule which does not coincide with its mirror image can be optically active. Moreover, for each optically active molecule one can always find another non-identical form of the same molecule which is related to the original molecule through reflection. These two forms of one molecule are called enantiomers, specifically $D-$ and $L-$ enantiomers, which naturally refer to the right- and left-handed forms, respectively. In many sources the D- and L-enantiomers of various molecules are discussed. However, it should be emphasized that currently there is no uniform relation between the absolute configuration of complex molecules and their ability to be left- and/or right-rotating. Here it is not our intention to summarize all basic rules found for numerous organic substances which are optically active. Instead, we restrict ourselves to an analysis relevant to observation of optical activity in the vacuum ultraviolet region.

The most interesting cases can be observed in various organic molecules, i.e. in molecules which include one or more carbon atoms. Formally, one carbon atom in a molecule which is bonded to four different atoms and/or groups of atoms is sufficient for manifestation of optical activity. In general, such a carbon atom is called an asymmetric atom, or a chiral center. In many cases the optical activity can be observed in molecules with two, three and more asymmetric carbon atoms (for more detail, see, e.g., [10], [11] and references therein). A very well known example is the tartaric acid which may exist in the form of D- and L-enantiomers and in its meso-form which has no optical activity. Note also that a number of organic molecules with no chiral centers show overall optical activity, e.g., allenes, spiranes and biphenyls. Such systems are considered as inherently dysymmetric. The active electrons in these molecules are delocalized over a chiral nuclear system.

In this work we restrict ourselves to the consideration of organic molecules with one asymmetric carbon atom (chiral center). In general, the observed optical rotation θ, Eq.(59),

produced by one asymmetric carbon atom in a molecule will be small. However, if some additional conditions are combined with each other, then the actual optical rotation θ increases to moderate, large and very large values. It was shown more than sixty years ago that 'close' presence of some special groups of atoms can increase the actual optical rotation by a few orders of magnitude. Such special groups are called 'chromophors'. Typical examples of chromophors are the $-NH_2$, $>CO$, $-CN$, $-C_6H_5$ groups and some others. It should be emphasized that none of these groups is optically active, but each amplifies significantly the optical activity of the neithbouring chiral center.

Currently, there are a few dozens of different atomic groups which are recognized as regular basic chromophors and a large number of special groups of atoms which become chromophors only at certain wavelengths. In general, any group of atoms which has excessive $\pi-$electron density can be considered as a potential chromophor and any experimental study of optical activity in organic molecules is reduced to the analysis of various chromophors and their influence on one of more asymmetric carbon atom(s). The problem contains many complications. For instance, if one of the hydrogen atoms in a benzene ring bonded with a chiral carbon center is replaced by the $-NH_2$ group, then one finds the new chromophor $-C_6H_4NH_2$ which has a different influence on this chiral center. In other words, the change in optical activity of the chiral center produced by the new chromophor ($-C_6H_4NH_2$) cannot be predicted accurately and uniformly from the analogous information known for the $-C_6H_5$ and $-NH_2$ groups. In general, the delocalization of $\pi-$electrons in various organic molecules can be used to create a huge number of 'new' chromophors. Moreover, if the same chiral center is bonded to both the $-C_6H_5$ and $-NH_2$ groups, the amplification of its chiral activity will be drastically different from the previous case. In addition to this one also finds that substitution of one hydrogen atom in the $-C_6H_5$ chromophor by, e.g., the $-CH_3$ group will also have a noticeable effect on overall optical activity. The following experimental analysis must detect (and investigate) a direct relation between the actual optical activity and position of the hydrogen atom (in the benzene ring) which was replaced by the $-CH_3$ group.

It is important for the general theory that each chromophore group can be represented by a number of poles located in the complex plane of frequencies ν (so-called ν-plane). In other words, any chromophore group has a number of poles in the complex ν-plane associated with it. If such a pole is close to the real axis, then in experiments one finds large and

very large values of optical rotation δ and circular dichroism κ, respectively. In real organic molecules one finds not one, but a few different chromophore groups. The experimental curves for the $\delta(\nu)$ and $\kappa(\nu)$ values measured for $\nu > 0$ in actual organic molecules are the result of interaction between various poles located in a complex frequency plane (ν) at different frequencies. In general, the interaction between different chromophores produces very complicated spectra for the optical rotation $\delta(\nu)$ and circular dichroism $\kappa(\nu)$. The complexity of these spectra rapidly increases as the number of poles per unit frequency interval increases. In particular, this is the case for vacuum ultraviolet wavelengths, since almost all known chromophors have many absorption lines located in VUV region.

VIII.   CONCLUSION

We have considered the phenomena of optical activity in homogeneous solutions of various organic substances. The classical macroscopic theory based on Maxwell equations in dielectric (or nonconducting) media is discussed in detail. The Stokes parameters for almost monochromatic light are defined rigorously. The relations between the optical rotation and circular dichroism are derived from the basic Kramers-Kronig relations. These relations allow one to obtain/evaluate, e.g., the circular dichroism by using the known values of optical rotation at the same frequencies. The explicit expression for the tensors of molecular optical activity are derived. Our formulas derived for the tensor(s) of molecular optical activity can be used to explain a large number of phenomenon currently known in molecular optical activity. Note that our formulas can successfully be applied to the case of the Raileigh (or non-shifted) scattering when $\omega_{21} = 0$ and also to the cases when $\omega_{21} \neq 0$ (shifted or combined light scattering). It is shown that all known lowest order effects of optical activity must be described with the use of finite number of tensors (five, three or one tensors).

We also briefly consider the quantum (or semi-classical) theory of molecular optical activity developed by Rosenfeld in [1]. In this theory all molecules are quantum systems, while all electromagnetic fields are described by classical Maxwell equations. A possibility to extend measurements of optical rotation and circular dichroism into the vacuum ultraviolet region is discussed. Currently, this task seems to be extremely difficult, since there are a large number of unsolved problems which must be considered before the whole procedure can be usefully implemented. Moreover, it is clear that even the requisite experimental

technique will have many fundamental differences from the technique applied for traditional wavelengths. Nevertheless, we can expect that measurements of optical rotation and circular dichroism in the vacuum ultraviolet region will produce a large volume of very valuable experimental data. These measurements will open a new avenue for some important discoveries and improvements in our current understanding of optical activity of organic molecules.

Acknowledgments

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