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Circular Dichroism in Dimer of Channelrhodopsin

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Abstract. The paper treats the excitonic model of channelrhodopsin (ChR) which consists of dimers, each one connected with two-fold symmetry axis. By using the general theory of molecular excitons and the studies of bacteriorhodpsin (BR), the tensors of dielectric permeability and the gyration tensor are calculated including the contributions of the molecular gyrotropy and of the excitonic coupling. Two cases of refraction in the membrane of ChR are studied: a) normal incidence; b) oblique incidence. The components of refracted waves and the shape of the signal of circular dichroism (CD) are analyzed. The CD spectrum of ChR exhibits a negative couplet in those two cases unlike the case of BR in which couplet disappears at normal incidence.

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1 Introduction

In this paper we explore a theoretical model of circular dichroism (CD) in a dimer of channelrhodopsin (ChR). The description of CD follows the model of bacteriorodhopsin [1] inspired by experimental and theoretical studies of that phenomenon in BR [2] and in ChR [3]. Our approach is based on the general theory of the molecular excitons [4, 5] and on its applications in organic solids [6]. The theoretical model includes the formalism of gyration tensor and of dielectric permeability taking into account the symmetry of dimer of ChR (point group C_2). Comparing the studies of BR with its two-dimensional hexagonal lattice of trimers (point group C_3), the low symmetry of ChR complicates the structure of the tensor of dielectric permeability and of the gyration tensor. The spectra of both materials in visible region are dominated by the strong transition of retinal chromophore. The CD spectra of BR and ChR contain a negative couplet centered at the transition frequency. But a remarkable difference appears at normal incidence of light on membranes: in CD spectrum of BR this negative couplet is replaced by one positive maximum only [2]. The authors of paper [3] do not announce such change of CD signal and this is a result of low symmetry of ChR dimer.

The paper outline is the following: Section 2 contains calculations of the gyration tensor components of the ChR dimer. In Section 3 we treat the refraction of electromagnetic waves (e.m.w.) at the boundary of ChR membrane in two cases, notably normal incidence and oblique incidence of e.m.w., and analyze the CD signal. Section 4 is concluding.

2 Dielectric Permeability and Gyration Tensor of ChR Dimer

The dimer of ChR consists of two identical moieties – monomers a and b, which can be reproduced using two-fold symmetry axis $\hat{z}$. Let $r_{O\alpha}$ ($\alpha = a, b$) is the distance from the two-fold axis $\hat{z}$ to the center of the retinal chromophore ($r_{Oa} = -r_{Ob}$). Following Ref. [3] we choose axis $\hat{y}$ to connect the two centers and axis $\hat{x}$ as right-handed coordinate partner ($\hat{x}\,\hat{y}\,\hat{z}$). The electronic excitations of retinal ChR possesses exciton energy $E_F = \hbar\omega_F$ ($\lambda \approx 470$ nm) and transition electric dipole moments, correspondingly:

$$\begin{aligned} \vec{\mu}_a &= \mu(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)\,, \\ \vec{\mu}_b &= \mu(-\sin\theta\cos\varphi, -\sin\theta\sin\varphi, \cos\theta)\,, \end{aligned} \tag{1}$$

where θ is the angle between the axis $\hat{z}$ and the direction of the transition moments $\vec{\mu}_a$ and $\vec{\mu}_b$; and φ is the angle between axis $\hat{x}$ and the projection of the transition moment μ_a on (xy)-plane. By using dipole-dipole intermonomer coupling and the usual procedure for treating the excitonic states, one obtains the following two dimer states [4–6]:

a) z-state with energy $E_1 = E_F + J$ and transition dipole moment $\vec{\mu}_a + \vec{\mu}_b$;
b) (xy)-state with energy $E_2 = E_f - J$ and transition dipole moment $\vec{\mu}_a - \vec{\mu}_b$.

The quantity J is the coupling energy of the two electric dipoles $\vec{\mu}_a$ and $\vec{\mu}_b$ spaced at distance $\Delta y = 2r_{Oa}$.

We reproduce (see the Appendix and Ref. [1]) the formalism of dielectric permeability in gyrotropic media $\varepsilon_{lm}(\omega, \vec{k})$, namely

$$\varepsilon_{lm}(\omega, \vec{k}) = \varepsilon^{(1)}_{lm}(\omega) + i\sum_{ns}\epsilon_{lns}\rho_{sn}(\omega)k_n + O(k^2)\,, \tag{2}$$

where ϵ_{lns} is the Levi-Chivita unit tensor and ρ_{sn} is the gyration tensor. In our case, we prefer to transform coordinate system $(x, y, z))$ to $(x', y', z \equiv 1, 2, 3)$ and choose the axis $\hat{x'}$ along the projection of transition dipole moment $\vec{\mu}_a$ and the $\hat{y'}$ perpendicular to $\hat{x'}$ and $\hat{z}$. Then one obtains the following components of the tensor $\varepsilon^{(1)}_{lm}(\omega)$ which describes the linear absorbtion:

$$\varepsilon_{11}(\omega) = a_1 - A\frac{\mu^2\sin^2\theta}{\hbar\omega - E_2}\,; \quad \varepsilon_{22} = a_2\,; \quad \varepsilon_{33} = a_3 - A\frac{\mu^2\cos^2\theta}{\hbar\omega - E_1}\,, \tag{3}$$

where $A = 4\pi/V$; V is the volume occupied by one dimer; and a_1, a_2, a_3 denote the contributions of other electronic resonances.

The components of the gyration tensor ρ represent sums of intrinsic molecular chirality $\vec{\mu} \cdot \vec{M}$ ($i\vec{M}$ is the transition magnetic moment of the same transition E_F in the molecules) and of the chiral excitonic coupling. The estimations in Refs. [2, 3] exhibit the dominant role of the excitonic coupling. The transition magnetic moments $\vec{M}_{a,b}$ of the moieties of the dimer can be written in a similar way as transition electric dipole moments (1) with M instead of μ and θ_M, φ_M replace θ, φ. Then for the components of gyration tensor we find the following expressions:

$$\rho_{11} = -\frac{2\mu M A}{\hbar\omega - E_1}\cos\theta\cos\theta_M\,, \quad \rho_{12} = 0\,, \tag{4a}$$

$$\rho_{21} = -\frac{2\mu M A}{\hbar\omega - E_2}\sin\theta\sin\theta_M\sin(\varphi-\varphi_M) - A\mu^2 r_{Oa}\sin 2\theta\sin\varphi\Big(\frac{1}{\hbar\omega - E_1} - \frac{1}{\hbar\omega - E_2}\Big), \tag{4b}$$

$$\rho_{22} = -2\mu M A\Big[\frac{\cos\theta\cos\theta_M}{\hbar\omega - E_1} + \frac{\sin\theta\sin\theta_M\cos(\varphi-\varphi_M)}{\hbar\omega - E_2}\Big] - A\mu^2 r_{Oa}\sin 2\theta\cos\varphi\Big(\frac{1}{\hbar\omega - E_1} - \frac{1}{\hbar\omega - E_2}\Big), \tag{4c}$$

$$\rho_{33} = -\frac{A\mu M}{\hbar\omega - E_2}\sin\theta\sin\theta_M\cos(\varphi-\varphi_M), \tag{4d}$$

$$\rho_{13} = \rho_{23} = \rho_{31} = \rho_{32} = 0\,. \tag{4e}$$

The chiral excitonic coupling ($\sim \mu^2$) enters the components ρ_{21} and ρ_{22} with more complicated frequency dependence. The estimations in Ref. [3] based on excitonic theory give the value of angle $\varphi = 104.22^\circ$ and hence $|\cos\varphi| \gg |\sin\varphi|$, which emphasizes the more important role of the ρ_{22} component.

3 Refraction of e.m.w. in a Membrane of ChR

Reflection and refraction of e.m. waves at the boundaries of gyrotropic media exhibit peculiarities connected with the constitutive relations $D(E)$ and $B(H)$ and correspondingly with the boundary conditions, see, e.g., Ref. [7] (D is dielectric displacement, B is magnetic induction). In the following we consider two cases of incident e.m.w. on the membrane of dimers: (i) normal incidence; and (ii) oblique incidence. In both cases the procedure of treating refraction and CD is relatively lengthy and consists of several steps:

a) by using Maxwell equations and material connections

$$D_l(\omega,\vec{k}) = \sum_m \varepsilon_{lm}(\omega,\vec{k})E_m(\omega,\vec{k})\,, \tag{5}$$

one finds the electromagnetic modes in the membrane;

b) applying correct boundary conditions we calculate the amplitudes of those electromagnetic modes depending on the amplitudes of incident e.m.w. ($E_1(\omega)$, $E_2(\omega)$) at normal incidence and (E_s, E_p) at oblique incidence;

c) calculations of common energy density of the two e.m. waves which propagate through the membrane;

d) we calculate CD signal as difference of absorbed energy density $u_+ - u_-$ of the incident e.m.w. with $E_2(\omega) \pm iE_1(\omega)$ (Section 3.1) and $E_p = \pm iE_s$ (Section 3.2. The absorption is related with the excitonic damping which is expressed by introducing the imaginary part in excitation energy $E_F + i\delta$.

3.1 Normal incidence ($k_1 = k_2 = 0$)

Two e.m. modes propagate in the membrane:

a) the mode with refractive index $n_1 = \sqrt{\varepsilon_{11}}$ and components $E_1(1)$ and $E_2(1) = i\rho_{33}[n_1^2/(\varepsilon_{22} - \varepsilon_{11})]E_1(1)$;

b) the mode of refractive index $n_2 = \sqrt{\varepsilon_{22}}$ and components $E_2(2)$ and $E_1(2) = i\rho_{33}[n_2^2/(\varepsilon_{22} - \varepsilon_{11})]E_2(2)$.

Solving the boundary problem, one obtains

$$E_1(1) = E_1(\omega)\frac{2n}{n + n_1 + i\rho_{21}} + iE_2(\omega)\frac{2n}{(n + n_1)(n + n_2)} \times \left[\frac{\rho_{33} + \rho_{11} - \rho_{22}}{2} + \rho_{33}\varepsilon_{22}\frac{n + n_2}{(\varepsilon_{22} - \varepsilon_{11})n_2}\right], \tag{6a}$$

$$E_2(2) = -iE_1(\omega)\frac{2n}{(n + n_1)(n + n_2)}\left[\frac{\rho_{33} - \rho_{11} + \rho_{22}}{2} + \frac{\rho_{33}\varepsilon_{11}(n + n_1)}{(\varepsilon_{22} - \varepsilon_{11})n_1}\right] + E_2(\omega)\frac{2n}{n + n_2}\,, \tag{6b}$$

where n is the refractive index of the outer medium which is supposed to be isotropic and non-gyrotropic, and $E_1(\omega)$, $E_2(\omega)$ are the components of the incident e.m.w.

In calculation of CD signal the case $E_2(\omega) = \pm iE_1(\omega)$ leads to the following expression for the energy density difference:

$$u_+ - u_- = \frac{32n^2|E_1(\omega)|^2}{(n + n_1)(n + n_2)}\left\{(\rho_{11} - \rho_{22})\left(\frac{\varepsilon_{11}}{n + n_1} + \frac{\varepsilon_{22}}{n + n_2}\right) + \rho_{33}\left[\frac{\varepsilon_{11}}{n + n_1} - \frac{\varepsilon_{22}}{n + n_2} + \frac{n_1n_2(n_1n_2 - n^2)}{(n_1 + n_2)(n_+n_1)(n + n_2)}\right]\right\}. \tag{7}$$

Expression (7) exhibits the difference of manifestation of CD in point groups C_2 and C_3. The higher symmetry of group C_3 demands $\rho_{11} = \rho_{22}$ and at the normal

incidence the CD signal depends on the component ρ_{33} only (see Ref. [1]). This component in both groups does not depend on the chiral excitonic contribution. However, in the case under consideration in point group C_2, the components $\rho_{11} \neq \rho_{22}$ and the component ρ_{22} only depends on $(\mu_a\mu_b)$-contribution (see Eq. (4c)). All molecular contributions to the gyrotropy which are proportional to (μM), see Eqs. (4), and their magnitude according to estimations in [2,3] is one order smaller than the magnitude of the chiral excitonic contribution. Moreover, the frequency dependence of CD molecular contributions (μM) in (4) (supposing that energy levels $(E_1,\ E_2)$ posses imaginary part $(i\delta)$) is of the type of Lorentzians with one maximum only. Frequency dependence of the excitonic contribution can be expressed with imaginary part of the difference (see (4c))

$$\mathrm{Im}\Big[\frac{1}{\hbar\omega-(E_F+J)-i\delta}-\frac{1}{\hbar\omega-(E_F-J)-i\delta}\Big] = \frac{2\delta(E_F-\hbar\omega)(E_1-E_2)}{[(\hbar\omega-E_1)^2+\delta^2][(\hbar\omega-E_2)^2+\delta^2]}\,. \tag{8}$$

Taking into account the strong inequality $\delta \gg |J|$ (see [2, 3] for the width of spectral line of the transition of retinal), expression (8) can be represented as proportional to the quantity

$$[\mathrm{CD}] \sim \frac{4J\delta(E_F-\hbar\omega)}{[(\hbar\omega-E_F)^2+\delta^2]^2}\,. \tag{9}$$

This expression is similar to CD signal in BR but at oblique incidence only [1]. In ChR expression (9) describes negative couplet in CD spectra both for oblique and normal incidence.

3.2 Oblique incidence ($k_1 = 0$; $k_2,\ k_3 \neq 0$)

Let the plane of incidence is ($y' \equiv 2$, $z \equiv 3$) and θ is the angle od incidence in outer medium. Then two refracted e.m. waves propagate in the membrane (the case $k_1 \neq 0$ is analogous *mutatis mutandis*):

a) e.m.w. of refractive index $n_{\mathrm{o}}^2 = \varepsilon_{11}$ which can be treated as "ordinary" as it is in the case of uniaxial media. Its electric components are $E_{1\mathrm{o}}$,

$$\begin{aligned} E_{2\mathrm{o}} &= i\frac{\rho_{33}(\varepsilon_{33}-k_{2\mathrm{o}}^2)k_{3\mathrm{o}}-\rho_{22}k_{2\mathrm{o}}^2k_{3\mathrm{o}}}{\varepsilon_{22}\varepsilon_{33}-\varepsilon_{22}k_{2\mathrm{o}}^2-\varepsilon_{33}k_{3\mathrm{o}}^2}E_{1\mathrm{o}}\,,\\ E_{3\mathrm{o}} &= i\frac{\rho_{22}(\varepsilon_{22}-k_{3\mathrm{o}}^2)k_{2\mathrm{o}}-\rho_{33}k_{3\mathrm{o}}^2k_{2\mathrm{o}}}{\varepsilon_{22}\varepsilon_{33}-\varepsilon_{22}k_{2\mathrm{o}}^2-\varepsilon_{33}k_{3\mathrm{o}}^2}E_{1\mathrm{o}}\,, \end{aligned} \tag{10}$$

where $(0,\ k_{2\mathrm{o}},\ k_{3\mathrm{o}})$ are the components of wave vector of this e.m. mode, and φ_{o} is its angle of refraction;

b) "extraordinary" e.m.w. of refractive index

$$n_{\mathrm{e}}^2 = \frac{\varepsilon_{22}\varepsilon_{33}}{\varepsilon_{22}\sin^2\alpha + \varepsilon_{33}\cos^2\alpha}\,, \tag{11}$$

where α is its angle of refraction. Its electric components are ($E_{1\mathrm{e}}$, $E_{2\mathrm{e}}$, $E_{3\mathrm{e}}$), correspondingly

$$\begin{aligned} E_{2\mathrm{e}} &= -\frac{\varepsilon_{33}k_{3\mathrm{e}}}{\varepsilon_{22}k_{2\mathrm{e}}}E_{3\mathrm{e}}\,, \\ E_{1\mathrm{e}} &= i\frac{1}{\varepsilon_{11}-n_{\mathrm{e}}^2}\Big[\rho_{22}k_{2\mathrm{e}} + \rho_{33}\frac{\varepsilon_{33}k_{3\mathrm{e}}^2}{\varepsilon_{22}k_{2\mathrm{e}}}\Big]E_{3\mathrm{e}}\,, \end{aligned} \tag{12}$$

where (0, $k_{2\mathrm{e}}$, $k_{3\mathrm{e}}$) are the components of wave vector of extraordinary e.m.w.

Solving boundary problem by using correct boundary conditions (see [7]), one obtains the following amplitudes:

$$E_{1\mathrm{o}} = ME_s + i\eta E_p\,; \quad E_{3\mathrm{e}} = NE_p + i\eta_{\mathrm{e}}E_s\,, \tag{13}$$

where (E_s, E_p) are the components of incident e.m.w. correspondingly perpendicular and parallel to the plane of incidence, and

$$M = \frac{-2n\cos\theta}{n_{\mathrm{o}}\cos\varphi_{\mathrm{o}} + n\cos\theta + i\rho_{21}}\,, \quad N = \frac{2n\cos\theta}{\Big(\dfrac{\varepsilon_{33}}{\varepsilon_{22}k_{2\mathrm{e}}}\Big)(nk_{3\mathrm{e}} + \varepsilon_{22}\cos\theta)}\,, \tag{14}$$

$$\eta = \frac{2n\cos\theta}{D_1}\Big[\frac{\rho_{11}+\rho_{33}-\rho_{22}}{2}\,\frac{\varepsilon_{33}k_{3\mathrm{e}}}{\varepsilon_{22}k_{2\mathrm{e}}} + \frac{k_{3\mathrm{e}}+n\cos\theta}{\varepsilon_{11}-k_{2\mathrm{e}}^2-k_{3\mathrm{e}}^2}\Big(\rho_{22}k_{2\mathrm{e}} + \rho_{33}\frac{k_{3\mathrm{e}}^2}{\varepsilon_{22}k_{2\mathrm{e}}}\Big)\Big], \tag{15}$$

$$\begin{aligned} \eta_{\mathrm{e}} = \frac{2n\cos\theta}{D_1}\Big\{&\frac{\rho_{22}-\rho_{11}+\rho_{33}}{2}\cos\theta \\ &+ \frac{1}{\varepsilon_{22}\varepsilon_{33}-\varepsilon_{22}k_{2\mathrm{o}}^2-\varepsilon_{33}k_{3\mathrm{o}}^2}\big[\rho_{22}k_{2\mathrm{o}}^2(\varepsilon_{22}\cos\theta + nk_{3\mathrm{o}}) \\ &- \rho_{33}k_{3\mathrm{o}}(\varepsilon_{33}k_{3\mathrm{o}}\cos\theta + n(\varepsilon_{33}-k_{2\mathrm{o}}^2)\big]\Big\}, \end{aligned} \tag{16}$$

$$D_1 = \frac{\varepsilon_{33}}{\varepsilon_{22}k_{2\mathrm{e}}}(nk_{3\mathrm{e}} + \varepsilon_{22}\cos\theta)(n_{\mathrm{o}}\cos\varphi_{\mathrm{o}} + n\cos\theta + i\rho_{21})\,. \tag{17}$$

For energy density of each e.m.w. (o- or e-), one obtains, see Ref. [7]:

$$u = \varepsilon_{11}|E_1|^2 + \varepsilon_{22}|E_2|^2 + \varepsilon_{33}|E_3|^2 - i\rho_{21}E_1H_2(\omega/c)\,, \tag{18}$$

where H_2 is the component of its magnetic field, c is the light velocity.

In the case of CD at $E_p = \pm iE_s$, we find the following difference of common energy density of both refracted e.m. waves:

$$u_+ - u_- = \frac{|E_s|^2}{\pi}\Big[\varepsilon_{11} M\eta + N\eta_{\mathrm{e}} \frac{\varepsilon_{33}^2}{n^2 \sin^2\theta}\Big]. \tag{19}$$

In the case of oblique incidence the impact of the intrinsic molecular gyrotropy and of the chiral excitonic coupling can be evaluated analyzing the frequaency dependence of the components ρ_{11}, ρ_{22}, ρ_{33} of the gyration tensor. Surely, this procedure is more complicated than the case of normal incidence (compare expression (7) and (19)). The most valuable contribution as well as appearing of the negative couplet in CD spectrum are done via component ρ_{22} which contained excitonic coupling and consequently the frequency dependence proportional to the quantity (9). It enters the expressions for η and η_{e} as the sums of difference $\rho_{22} - \rho_{11}$ (as it is in the case of normal incidence) and of two other terms proportional to ρ_{22}.

4 Conclusions

The general theory of molecular excitons is applied in the paper for the case of a dimer with two-fold symmetry axis. This model of channelrhodopsin describes its absorbtion and CD spectra in visible region. The comparison of the models of ChR and bacteriorhodopsin shows the similarities of the structure of their dielectric permeability and gyration tensor and the different shapes of CD spectra at normal incidence caused by the difference of symmetry (low symmetry of ChR and uniaxial symmetry of BR).

An interesting feature of the spectra of ChR is demonstration of vibronic wings (not existing in BR). Their theoretical tretment can be the topic of another study if the experimental data for their shape would be more detail.

A Formalism of Dielectric Permeability Tensor in Gyrotropic Media

Tensor $\varepsilon_{lm}(\omega, \vec{k})$ connects electric field vector $\vec{E}(\omega, \vec{k})$ and vector $\vec{D}$ of electric displacement, see formulas (5) and (2). Tensor $\varepsilon_{lm}(\omega, \vec{k})$ can be calculated using the formalism of Green functions calculated at temperature $T = 0$, namely [4,5]

$$\varepsilon_{lm}(\omega, \vec{k}) = \delta_{lm} - \frac{4\pi}{\omega^2 \hbar V} \langle \hat{J}_l(\vec{k}, t) \hat{J}_m(-\vec{k}, t') \rangle_\omega \,, \tag{A.1}$$

where δ_{lm} is the unit tensor, V is the volume of the medium, and the last term is the Fourier component (lm) of the retarding Green functions of the linear momentum operator $\hat{J}$ of all electric charges in the medium. Near the frequency

of the electronic resonances $\hbar\omega_F$, the main contribution in operator $\hat{J}$ comes from the electrons.

Let $\alpha = a, b$ is the number of dimer monomers and $B_{\alpha\vec{n}}$ is the operator of annihilation of the excitation of monomer α (we treat the retinal excitations) which is a part of dimer situated at node $\vec{n}$ of the membrane. Then the operator $\hat{J}(\vec{k})$ can be represented as a sum of the following two operators [6, 8]:

$$\hat{J}_l^{(1)}(\vec{k}) = i\sum_{\alpha}\mu_{\alpha}^{(l)}\omega_F[-B_{\alpha}(\vec{k}) + B_{\alpha}^{+}(\vec{k})], \tag{A.2}$$

$$\hat{J}_l^{(2)}(\vec{k}) = \sum_{s\alpha j} k_s\omega_F[B_{\alpha}(\vec{k}) + B_{\alpha}^{+}(\vec{k})][r_{0\alpha}\mu_{\alpha}^{(l)} + \epsilon_{lsj}M_{\alpha}^{(j)}], \tag{A.3}$$

where $B_{\alpha}(\vec{k})$ is k-representation of $B_{\alpha\vec{n}}$, $\vec{\mu}_{\alpha}$ and $(i\vec{M}_{\alpha})$ are the transition electric dipole and transition magnetic dipole moments of the monomer α, whereas $\vec{r}_{0\alpha}$ is the equilibrium position of chromophores in the same monomer. We calculate the components of the tensor $\varepsilon(\omega, \vec{k})$ using formulas (A.1)–(A.3) and obtain the tensors (3) and (4) for the dimer of ChR.

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