Exciton-Phonon Interaction in Optical Rotation

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Effects of exciton-phonon interaction on optical rotation and refractive index of a polymer are investigated on the basis of the Frenkel exciton model. Exciton-phonon interaction has a little effect on optical rotation and refractive index in comparison with that exerted by electron-electron interaction between monomers, as far as the Frenkel exciton model is concerned. When exciton-phonon interaction is negligible and intermonomeric interaction is much less than exciton energy, the optical rotatory dispersion has the anomalous term; however, the anomalous dispersion disappears in the absorption of light. A relation between rotational angle and refractive index is derived.

1. Introduction

One of the present authors (T. A.)1) developed the microscopic theory of optical rotation on the basis of the linear response theory and applied it to a long helical polymer by using the Frenkel exciton model. In that theory, vibrations of monomers are neglected, that is, the indirect intermonomeric interaction through phonons is neglected.

In most of the theoretical investigations of optical rotation, temperature-dependent optical rotation formulae have been derived by the perturbation theory through introducing the Boltzmann distribution over energy levels.2) As in the BCS theory of superconductivity, electron-electron interaction through phonons may give rise to the temperature dependence of optical rotation.

In the present paper, we investigate the effect of exciton-phonon interaction on optical rotation and refractive index in a linear polymer.

In sec. 2 we make the total Hamiltonian of the polymer on the basis of the molecular exciton model by using the second quantization technique. In sec. 3 formulae for optical rotation and refractive index are derived in terms of response function as the commutator of exciton annihilation and creation operators. In sec.

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we obtain response functions by the Green function method. It has been proved that exciton-phonon interaction has a little effect on optical rotation and refractive index as far as the Frenkel exciton model is concerned. We have found that rotational angle is closely related to refractive index. Section 5 is devoted to discussion.

2. Hamiltonian

The system under consideration is a polymer composed of similar monomers. The total Hamiltonian $\mathcal{H}$ of the system is expressed as

$$\mathcal{H} = \sum_n \mathcal{H}_n + \frac{1}{2} \sum_{n,m} \sum_{i,j} V_{nm}(r_{in} - r_{jm}) + \sum_n \sum_{m \neq n} v(r_{in} - R_m),$$

(1)

where $r_{in}$ is the coordinate of the $i$th electron in the $n$th monomer in the polymer, $R_m$ the coordinate of the centre of the $m$th monomer (for example, that of the nucleus of the $m$th monomer), $\mathcal{H}_n$ the Hamiltonian of the $n$th isolated monomer, $V_{nm}(r_{in} - r_{jm})$ the interaction between the $i$th electron in the $n$th monomer and the $j$th electron in the $m$th monomer and $v(r_{in} - R_m)$ is the interaction between the $i$th electron in the $n$th monomer and the nucleus of the $m$th monomer.

In order to derive phonons, taking an average over the positions of electrons in intermonomeric interaction $V_{nm}$, we obtain

$$V_{nm}^{\alpha\beta\gamma\delta}(R_{n} - R_{m}) = \int \, dr_{in} \int \, dr_{jm} \varphi_{n\alpha}^*(r_{in}) \varphi_{m\beta}^*(r_{jm}) V_{nm}(r_{in} - r_{jm}) \times \varphi_{m\gamma}(r_{jn}) \varphi_{n\delta}(r_{jm}),$$

(2)

where $\varphi_{n\alpha}(r_{in})$ is the $\alpha$-state function of the $i$th electron in the $n$th monomer. We consider the linear polymer, composed of $N$ similar monomers spaced a distance $d$ apart on the $z$-axis, and small vibrations of monomers along the $z$-axis. Let us define a displacement $u_n$ as the displacement of the $n$th monomer from its equilibrium position $R_n^{\circ}$, that is, $R_n = R_n^{\circ} + u_n$, and then $V_{nm}^{\alpha\beta\gamma\delta}$ may be expanded as a power series in displacement $u_n$ around the equilibrium position $R_n^{\circ}$ as follows:

$$V_{nm}^{\alpha\beta\gamma\delta}(R_{n} - R_{m}) = V_{nm}^{\alpha\beta\gamma\delta}(R_n^{\circ} - R_m^{\circ})$$

$$+ \frac{1}{2} \left( \frac{\partial^2 V_{nm}^{\alpha\beta\gamma\delta}}{\partial R_n^{\circ 2}} \right)_0 (u_n - u_m)^2 + \cdots,$$

(3)

We can derive phonons from the harmonic term in eq. (3) and the kinetic energy part of $\mathcal{H}_n$ in eq. (1) by the operator technique. Introducing a Fourier
transformation to the following set of new operators, derived from operators $u_n(t)$ and $p_n(t)$, the momentum of the $n$th monomer,

$$U_k(t) = \frac{1}{\sqrt{N}} \sum_n e^{iknd}u_n(t),$$

$$P_k(t) = \frac{1}{\sqrt{N}} \sum_n e^{-iknd}p_n(t),$$

one may diagonalize the Hamiltonian of phonons in the form

$$\mathcal{H}_\nu = \frac{1}{2M} \sum_k P_k \hat{P}_k + \frac{M}{2} \sum_k (\omega(k))^2 U_k \hat{U}_k,$$  

where $M$ denotes the mass of the monomer and

$$M(\omega(k))^2 = \tilde{V}(0) - \tilde{V}(k)$$

$$\tilde{V}(k) = \sum_{n-m=0}^{N-1} \frac{\partial^2 V_{nm\alpha \beta \gamma \delta}}{\partial R_n^2} (\frac{\omega(k)}{M})^2.$$  

Let us define the following annihilation and creation operators for phonons:

$$b_k = \frac{1}{\sqrt{2M\omega(k)}} (P_k - iM\omega(k)U_k),$$

$$b_k^\dagger = \frac{1}{\sqrt{2M\omega(k)}} (P_k^\dagger + iM\omega(k)U_k).$$

Equation (5) can be expressed, by use of eq. (7), as

$$\mathcal{H}_\nu = \sum_k K_{\omega(k)} \left( b_k b_k^\dagger + \frac{1}{2} \right).$$  

It is verified by using the commutation relations for $u_n$ and $p_n$ that the operators $b_k$ and $b_k^\dagger$ satisfy the following commutation relations

$$[b_k, b_{k'}^\dagger] = \delta_{kk'}, \quad [b_k, b_{k'}] = 0, \quad [b_k^\dagger, b_{k'}] = 0.$$

The last term in eq. (1) gives rise to exciton-phonon interaction. If we expand $v(r_{in} - R_m)$ in a power series in $u_m$, we find that

$$v(r_{in} - R_m) = v(r_{in} - R_m^0) - \left( \frac{\partial v}{\partial R_m} \right) u_m + \cdots,$$  

and the electron-phonon interaction is obtained from the second term on the right-hand side of eq. (10) in the form
\[ \mathcal{H}_{\text{el-ph}} = \sum_k \sum_n \sum_{\alpha \beta} v^{n\alpha\beta}(k) \frac{1}{\sqrt{N}} \sum_n e^{-iknd} a_{n\alpha} \dagger a_{n\beta} (b_k \dagger - b_{-k}), \]  

where \( a_{n\alpha} \) and \( a_{n\alpha} \dagger \) are the annihilation and the creation operator for the \( \alpha \)-state electron in the \( n \)th monomer, respectively, and

\[ v^{n\alpha\beta}(k) = \frac{1}{i} \sqrt{\frac{1}{2\hbar \omega(k)}} \sum_{n-m} e^{ik(n-m)d} \times \int dr_i \varphi_{n\alpha}(r_i) (-1) \left( \frac{\partial v}{\partial R_m} \right) \varphi_{n\beta}(r_i). \]

We investigate the effect of phonon on optical rotation by making use of the Frenkel exciton model of polymer. To derive exciton-phonon interaction, it is convenient to make a Fourier transform

\[ B_{kf} = \frac{1}{\sqrt{N}} \sum_n e^{-iknd} B_{nf}, \]
\[ B_{kf} \dagger = \frac{1}{\sqrt{N}} \sum_n e^{iknd} B_{nf} \dagger \]

where \( B_{nf} \) and \( B_{nf} \dagger \) are the annihilation and the creation operator for the exciton at the \( n \)th monomer and of the \( f \)th level, respectively, i.e. \( B_{nf} = a_{nf} \dagger a_{nf} \) and \( B_{nf} \dagger = a_{nf} \dagger a_{nf} \). Thus, the exciton-phonon interaction is given by

\[ \mathcal{H}_{\text{el-ph}} = \sum_f \sum_k v_f(k) (B_{-kf} \dagger + B_{kf})(b_k \dagger - b_{-k}) \]

with the commutation relations for \( B_{kf} \) and \( B_{kf} \dagger \)

\[ [B_{kf}, B_{k'f} \dagger ] = \delta_{kk'} \delta_{ff'}, \quad [B_{kf}, B_{k'f}] = 0, \quad [B_{kf} \dagger, B_{k'f} \dagger] = 0, \]

where \( v_f(k) = v^{nf}(k) \) with superscript 0 denoting the ground state of electron.

By making use of eq. (13) the Hamiltonian including no phonon part is expressed in terms of \( B_{kf} \) and \( B_{kf} \dagger \) by second quantization. \(^1\)

Finally, the total Hamiltonian of the polymer becomes

\[ \mathcal{H} = [E_0 + \sum_f \sum_k \Delta_f B_{kf} \dagger B_{kf} + \frac{1}{2} \sum_f \sum_k V_f(k) (B_{-kf} \dagger + B_{kf})(B_{kf} \dagger + B_{-kf})] \]
\[ + \sum_f \hbar \omega(k) \left( b_k \dagger b_k + \frac{1}{2} \right) \]
\[ + \sum_f \sum_k v_f(k) (B_{-kf} \dagger + B_{kf})(b_k \dagger - b_{-k}) \]
under the conditions $\langle B_{hf}^\dagger B_{hf}\rangle \ll 1$ and $\sum_j B_{hf}^\dagger B_{hf} = 1$, where $E_g$ is the ground state energy, $\Delta_f$ the eigen energy of the $f$–state of monomer and $V_f(k)$ the Fourier transform of the interaction between monomers\(^1\) given by

$$V_f(k) = \sum_{n-m} e^{ik(n-m)}dV_{nmf}$$

$$V_{nmf} \equiv \int d\mathbf{r}d\mathbf{r}'\varphi_{hf}^\ast(r)\varphi_{m0}^\ast(r')V(r-r')\varphi_{m0}(r)\varphi_{mf}(r')$$

3. Formulation of Optical Rotation

Maxwell’s equations give the basic equation for optical rotation

$$q_z^2 - q_e^2 + \frac{1}{c^2} \left[ Q_D(q_z, \omega) + iQ_N(q_z, \omega) \right] = 0,$$

where $q_e = \omega/c$ and the upper (lower) sign corresponds to left (right) circularly polarized light. If we take the direction of propagation of an incident monochromatic light of frequency $\omega$ to be parallel to the $z$–axis, correlation functions $Q_D(q, \omega)$ and $Q_N(q, \omega)$ are expressed in terms of the spatial Fourier transform $j(q, t)$ of the electric current density operator in the form\(^1\)\(^,\)\(^5\)

$$Q_D(q, \omega) = \frac{2\pi i\omega}{V} \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(t) \int_0^\beta d\lambda \langle j_z(q, t)j_z(-q, i\hbar\lambda) \rangle + j_z(q, t)j_z(-q, i\hbar\lambda) \rangle$$

$$Q_N(q, \omega) = \frac{2\pi i\omega}{V} \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(t) \int_0^\beta d\lambda \langle j_z(q, t)j_z(-q, i\hbar\lambda) \rangle - j_z(q, t)j_z(-q, i\hbar\lambda) \rangle.$$

where $V$ denotes the volume of the system, $\theta(t)$ the step function, $\beta = (kT)^{-1}$ and the triangular bracket represents the canonical average, that is,

$$\langle \ldots \rangle = \frac{\text{Tr}[\exp(-\beta H)]}{\text{Tr}[\exp(-\beta H)]}.$$

When one expands $Q_D(q, \omega)$ and $Q_N(q, \omega)$ as a power series in the wave–number $q$ of light up to the first order in $q$ into
and when one defines refractive indices \( n_+ \) and \( n_- \), respectively, for left and right circularly polarized lights and the rotational angle \( \phi \) of the plane of polarization per unit path length* by

\[
\tilde{n} = \frac{q_- + q_+}{2} = q_0 \frac{n_- + n_+}{2}
\]

\[
\phi = \frac{q_- - q_+}{2}
\]

one obtains relations between \( \tilde{n} \) and \( \phi \) as follows:

\[
\tilde{n}^2 - \phi^2 = q_0^2 - \frac{1}{e^2} Q_D^{(0)}(0, \omega)
\]

\[
\phi = -\frac{i}{2e^2} Q_N^{(1)}(0, \omega)
\]

where use has been made of \( Q_D^{(1)}(0, \omega) = Q_N^{(0)}(0, \omega) = 0 \). It is shown that refractive index relates closely to rotational angle.

Let us suppose that the polymer has a pitch angle \( \varphi \) between adjacent monomers. The Fourier transform of the electric current density operator is represented in terms of \( B_n \) and \( B_n^\dagger \), under the assumption—without loss of generality—that the wave function is real, in the form

\[
j(q, t) = \sum_f \sum_{n=0}^{N-1} e^{iqn} e^{i\varphi} \mathcal{T}^n J(q)(B_n(t) - B_n^\dagger(t))
\]

with

\[
\mathcal{T}^n = \begin{bmatrix}
\cos n\varphi & -\sin n\varphi \\
\sin n\varphi & \cos n\varphi
\end{bmatrix}
\]

and

\[
J(q) = (J^{(0)}(q))_{f_0},
\]

where \( (J^{(0)}(q))_{f_0} \) is the matrix element of the electric current density operator \( J^{(0)}(q) \) for the zeroth monomer.

* The sense of rotation is defined so that positive \( \phi \) corresponds to counterclockwise rotation as seen by an observer against the \( z \)-direction.
Let us consider only the lowest exciton for the sake of simplicity. Substitution of eq. (24) into eqs. (19) and (20) leads to

\[ Q_D(q, \omega) = -\frac{\pi N \hbar \omega}{V A_f} \left\{ J_0(q) [G_{q+\frac{\omega}{\hbar}, f}^{(\theta)}(\omega) + G_{q-\frac{\omega}{\hbar}, f}^{(\theta)}(\omega)] \\
- i J_0(q) [G_{q+\frac{\omega}{\hbar}, f}^{(\theta)}(\omega) - G_{q-\frac{\omega}{\hbar}, f}^{(\theta)}(\omega)] \right\} \]

(25)

and

\[ Q_N(q, \omega) = -\frac{\pi N \hbar \omega}{V A_f} \left\{ J_0(q) [G_{q+\frac{\omega}{\hbar}, f}^{(\theta)}(\omega) + G_{q-\frac{\omega}{\hbar}, f}^{(\theta)}(\omega)] \\
+ i J_0(q) [G_{q+\frac{\omega}{\hbar}, f}^{(\theta)}(\omega) - G_{q-\frac{\omega}{\hbar}, f}^{(\theta)}(\omega)] \right\}, \]

(26)

where

\[ J_0(q) = J_x(q) J_x(-q) + J_y(q) J_y(-q) \]

(27)

and

\[ G_{h f}(\omega) = \sum_{n=-\infty}^{N-1} e^{i \hbar (n-m)d} \int_{-\infty}^{\infty} dt e^{-i \omega t} \frac{i}{\hbar} \theta(t) \]

\[ \times \langle [B_{nf f}(t) + B_{nf f}^*(t), B_{mf f}(0) - B_{mf f}(0)] \rangle. \]

(28)

4. Green Functions

Refractive index and optical rotation can be expressed by use of Green functions

\[ G_{h f}(\omega) = \int_{-\infty}^{\infty} dt e^{-i \omega t} G_{h f f}(t) \]

(29)

with

\[ G_{h f f}(t) = \frac{i}{\hbar} \theta(t) \langle [B_{hf}(t) \pm B_{hf}(t), B_{hf}(0) - B_{hf}(0)] \rangle, \]

(30)

as has been seen in eqs. (19), (20), (21), (23), (25) and (26). In course of calculating Green functions, one obtains an equation

\[ \frac{\hbar}{i} \frac{dG_{h f f}(t)}{dt} = 2 \delta(t) \pm A_f G_{h f f}(t) \]

(31)
by differentiating eq. (30) with respect to time t. If one takes the time derivative of \( G_{k \sigma}(t) \) on the right-hand side of eq. (31) in order to obtain \( G_{k \sigma}(t) \), one will have a Green function \( \mathcal{G}_{k \sigma}(t) \) of new type

\[
\mathcal{G}_{k \sigma}(t) = \frac{1}{\hbar} \theta(t) \langle [b_k(t) \pm b_{-k}(t), B_{k \sigma}(0) - B_{k \sigma}(0)] \rangle, \tag{32}
\]

which immediately allows \( \mathcal{G}_{k \sigma}(t) \) to be defined. Similarly, if one takes a series of time derivatives for these Green functions, one will obtain coupled equations of Green functions of various types. By solving these simultaneous equations for \( G_{k \sigma}(t) \) and \( \mathcal{G}_{k \sigma}(t) \), one can obtain

\[
G_{k \sigma}(\omega) = \frac{2\hbar \omega}{(\hbar \omega)^2 - \Delta_f \left( \Delta_f + 2V_f(\omega) - \frac{4(\hbar \omega(\omega))(V_f(\omega))^2}{(\hbar \omega)^2 - (\hbar \omega(\omega))^2} \right)}, \tag{33}
\]

Under the condition \( \hbar \omega(k) < \hbar \omega \), eq. (33) may be rewritten into

\[
G_{k \sigma}(\omega) = \frac{2\hbar \omega}{(\hbar \omega)^2 - \Delta_f (\Delta_f + 2V_f(\omega)) + 4\Delta_f (\hbar \omega(\omega)) \left( \frac{V_f(\omega)}{\hbar \omega} \right)^2}. \tag{34}
\]

Since \( V_f(\omega) \ll \hbar \omega \), the value of the third term in the denominator in eq. (34) is much less than those of the first and second terms. This states that there is a little effect of the exciton-phonon interaction on refractive index and optical rotation as far as the Frenkel exciton model is concerned.

When one neglects the exciton-phonon interaction, the Green function \( G_{k \sigma}(\omega) \) reduces to

\[
G_{k \sigma}(\omega) = \frac{2\hbar \omega}{(\hbar \omega)^2 - 2\Delta_f V_f(\omega)}, \tag{35}
\]

which has been given in ref. 1. In order to calculate \( Q_D(q, \omega) \) and \( Q_N(q, \omega) \) represented by eqs. (25) and (26), let us define the sum and remainder of Green functions up to the first order in \( q \) as follows:

\[
G_{\pm} \equiv G_{q, r_{k \sigma}}(\omega) \pm G_{q, -r_{k \sigma}}(\omega) = G_{\pm}^{(+)} + qG_{\pm}^{(1)}.	ag{36}
\]

Since \( J_0(q) \) in eqs. (25) and (26) has no linear term in \( q \) and \( J_1(q) \) in those equations has no constant term in \( q \), \( Q_D(q, \omega) \) and \( Q_N(q, \omega) \) reduce to

\[
\begin{align*}
Q_D(q, \omega) &= A [ J_0^{(+)}G_{+}^{(+)} ] \\
Q_N(q, \omega) &= Aq [ J_1^{(+)}G_{+}^{(+)} + iJ_0^{(+)}G_{-}^{(+)} ] \\
A &= - \frac{\pi N \hbar \omega}{V \Delta_f},
\end{align*}
\]

\[
\begin{cases}
Q_D(q, \omega) = A [ J_0^{(+)}G_{+}^{(+)} ] \\
Q_N(q, \omega) = Aq [ J_1^{(+)}G_{+}^{(+)} + iJ_0^{(+)}G_{-}^{(+)} ] \\
A = - \frac{\pi N \hbar \omega}{V \Delta_f}
\end{cases}
\tag{37}
\]

Since \( J_0(q) \) in eqs. (25) and (26) has no linear term in \( q \) and \( J_1(q) \) in those equations has no constant term in \( q \), \( Q_D(q, \omega) \) and \( Q_N(q, \omega) \) reduce to...
where $f^{(0)}_i = f^{(0)}_0$ and $f^{(1)}_i = qf^{(1)}_i$. Consequently, one may say that $Q_D(q, \omega)$ is independent of $q$ and that $Q_N(q, \omega)$ is proportional to $q$.

Furthermore, when we expand the Green function (35) in a power series in $V_f(k)$ as in ref. 1, then using eq. (17) and the expression

$$\frac{1}{[(\hbar \omega)^2 - A_i^2 - 2A_f \sum_{n \neq m} e^{i(n-m)q} V_{nmf}]^2}$$

we find out an expression

$$\frac{\partial G^{(0)}(k)}{\partial (\varphi/d)} = G^{(1)}(k).$$

By making use of this equation one can derive the relation between refractive index and optical rotation

$$\tilde{n} \frac{\partial \tilde{n}}{\partial (\varphi/d)} + C(\tilde{n}^2 - q^2) \phi \frac{\partial \phi}{\partial (\varphi/d)} + C\phi^2 - \phi,$$

where

$$C = -\frac{i}{2} \frac{f^{(1)}_0}{f^{(0)}_0}.$$
in the form of eq. (16) on the basis of the Frenkel exciton model.

In the optical frequency region it may be satisfied that $\hbar \omega(k) < \hbar \omega$, hence the Green function may be allowed to reduce to the form of eq. (34). Since the exciton-phonon interaction energy is much less than photon energy, the value of the third term in the denominator on the right-hand side of eq. (34) is negligibly small as compared with those of the other terms. This means that the exciton-phonon interaction has a little effect on refractive index and optical rotation.

As has been seen in eqs. (25) and (26), $Q_D(q, \omega)$ and $Q_N(q, \omega)$ are expressed in terms of $G_x$ defined by eq. (36), $J_0(q)$ and $J_1(q)$. In these expressions the roles of $J_0(q)$ and $J_1(q)$ are interchanged with each other in $Q_D(q, \omega)$ and $Q_N(q, \omega)$ that is, the anomalous dispersion relates to $J_1(q)$ in the absorption of light and to $J_0(q)$ in the optical rotation. When the effect of exciton-phonon interaction can be neglected, $Q_D(q, \omega)$ has no anomalous dispersion, whereas $Q_N(q, \omega)$ has the anomalous dispersion, because the anomalous dispersion term arises from the first order term of $q$, i.e. $G_x^{(1)}$ in eq. (37).

By expanding the Green function of eq. (35) in a power series in $V_f(k)$, we have found a relation between refractive index and optical rotational angle as expressed by eq. (39). Therefore, it has been seen that the optical rotation is in close connection with the refractive index or the absorption of light. The constant $C$ in eq. (39) corresponds to the gyration constant or the rotatory parameter $g_0$ given by the classical phenomenological theory of optical rotation developed in ref. 6.

References

2) See, for example, Ying-Nan Chiu, J. Chem. Phys., 52 (1970), 1042.
3) J. M. Ziman, Elements of Advanced Quantum Theory, Chap. 1, Cambridge Univ.