Optical Rotation for the Oriented Polymers

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A calculation of the optical rotatory dispersion of helical polymer for the incident light perpendicular to the helical axis has been carried out in terms of the linear response theory. The term added by Moffitt, Fitts and Kirkwood to Moffitt's result does not appear and the rotational strength contains explicitly the helical radius of the polymer. For the randomly oriented assembly of helical polymers the result botained by Moffitt, Fitts and Kirkwood is derived.

§ 1. Introduction

Recently Ando[1] discussed the optical rotation of a polymer for the light parallel to the helical axis. Experimentally it is interested in the differences of the optical rotatory power being arised for the various direction of light. Actually Tinoco[2] observed the differences of optical rotatory dispersion (O. R. D.) for the beam parallel or perpendicular to the helical axis. The optical rotation originates in the term of the first order of the wave number q of light. Using the adjacent distance d between chromophores, the optical rotation is of the order of qd which results from the phase difference between the adjacent chromophores. Since the interaction between chromophores propagates with the light velocity, it needs the time d/c for the change arised in a chromophore to arrive the adjacent chromophore.

Let us consider the light propagating along the z-direction, which is expressed by $\exp(i\omega t - iqz)$. Considering the time retardation for the interaction to propagate with the light velocity, the light should be expressed by $\exp(i\omega t - iqz - iqd)$ which deviates the factor $\exp(-iqd)$ compared with no retardation. It is not so clear that the effect is negligible compared with the effect of the phase difference $\exp(-iqd)$. In other word we may say that the optical rotation is too subtle phenomena to neglect the relativistic effect, especially the retardation-effect of interaction. However, it is very difficult to take into account of the retardation. It is the problem that the experiment agrees with the theory taking account of no retardation or does not. In order to investigate

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this problem, we calculate the optical rotation for the incident light perpendicular to the helical axis and compare with the results for the parallel case.

§ 2. The optical rotation in the case of light perpendicular to the helical axis

We consider the helical polymer which has the same chromophores with the adjacent distance d on the helical axis and the pitch angle φ. Since the light propagates along the z-direction, let us take the z-axis as the ζ-axis of the coordinate fixed on the polymer, the y-axis as the η-axis and the x-axis as the ξ-axis, which is the helical axis. When the relation

$$\eta = \eta' \cos n\varphi - \zeta' \sin n\varphi \tag{1}$$

$$\zeta = \eta' \sin n\varphi + \zeta' \cos n\varphi \tag{2}$$

is satisfied, the coordinate (ξ, η, ζ) is equivalent to the coordinate $(\xi - nd, \eta', \zeta')$.

As shown by Stephen[3], the O. R. D. is exressed as

$$Q(q, \omega) = 2\pi i\omega \sum_{n,m} \int_{-\infty}^{\infty} dt\theta(t) \int_0^\beta d\lambda < j_\xi^{(n)}(q, t - i\hbar\lambda) j_\eta^{(m)}(-q, 0)$$
$$- j_\eta^{(n)}(q, t - i\hbar\lambda) j_\xi^{(m)}(-q, 0) > e^{-i\omega t}, \tag{3}$$

where $j^{(n)}(q, t)$ represents the spatial Fourier component of the current operator of the n-th chromophore. Since the radius of the helical polymer is very small compared with the wave length λ of light, $\exp(iq\zeta)$ may be approximated by $(1 + iq\zeta)$. This approximation is not allowed in the case of light parallel to the helical axis, By making use of this approximation and assuming the exciton model, $j_\xi^{(n)}(q, t - i\hbar\lambda)$ is expressed, under the assumption that the wave function is real, as

$$j_\xi^{(n)}(q, t - i\hbar\lambda) = \left\{ (j_\xi^{(0)})_{f0} + \frac{e\hbar q}{m} \left[\left(\eta \frac{\partial}{\partial \xi} \right)_{f0}^{(0)} \sin n\varphi + \left(\zeta \frac{\partial}{\partial \xi} \right)_{f0}^{(0)} \cos n\varphi \right] \right\}$$
$$\times (B^+_{nf}(t - i\hbar\lambda) - B_{nf}(t - i\hbar\lambda)), \tag{4}$$

where B^+_{nf} and B_{nf} are the creation and the annihilation operators of the f-th excited state at the n-th chromophore, respectively, and the superscript (0) represents a standard chromophore. Here we have considered only the lowest excitation. Henceforth, the same symbols for physical quantities with those described in the reference 1) are used as far as no confusion arises. Similarly $j_\eta^{(n)}(-q, 0)$ is written as

$$j_\eta^{(n)}(-q,\ 0)=\left\{(j_\eta^{(n)})_{f0}-\frac{e\hbar q}{m}\left(\zeta\frac{\partial}{\partial\eta}\right)_{f0}^{(n)}\right\}(B^+_{nf}-B_{nf})$$

$$=\Big\{(j_\eta^{(0)})_{f0}\cos n\varphi-(j_\zeta^{(0)})_{f0}\sin n\varphi$$

$$-\frac{e\hbar q}{m}\Big[\left(\eta\frac{\partial}{\partial\eta}\right)_{f0}^{(0)}\sin n\varphi\cos n\varphi-\left(\eta\frac{\partial}{\partial\zeta}\right)_{f0}^{(0)}\sin^2 n\varphi$$

$$-\left(\zeta\frac{\partial}{\partial\zeta}\right)_{f0}^{(0)}\sin n\varphi\cos n\varphi+\left(\zeta\frac{\partial}{\partial\eta}\right)_{f0}^{(0)}\cos^2 n\varphi\Big]\Big\}(B^+_{nf}-B_{nf}). \qquad (5)$$

The superscripts (0) are omitted for the simplicity in what follows.

Introducing a Green function $G_{nm}(\omega)$

$$G_{nm}(\omega)=\frac{i}{\hbar}\int_{-\infty}^{\infty}dt\theta(t)\langle[B^+_{nf}(t)+B_{nf}(t),\ B^+_{mf}(0)-B_{mf}(0)]\rangle e^{-i\omega t}$$

and substituting (4) and (5) into (3), $Q(q,\ \omega)$ is given by

$$Q(q,\ \omega)=-\frac{2\pi\hbar\omega}{\Delta}\sum_n\sum_m\Big\{(j_\xi)_{f0}[(j_\eta)_{f0}(\cos m\varphi-\cos n\varphi)-(j_\zeta)_{f0}(\sin m\varphi-\sin n\varphi)]$$

$$+\frac{e\hbar q}{m}\Big[\left(\eta\frac{\partial}{\partial\xi}\right)_{f0}(j_\eta)_{f0}-\left(\zeta\frac{\partial}{\partial\xi}\right)_{f0}(j_\zeta)_{f0}\Big]\sin(n+m)\varphi$$

$$+\frac{2e\hbar q}{m}\Big[\left(\zeta\frac{\partial}{\partial\xi}\right)_{f0}(j_\eta)_{f0}\cos n\varphi\cos m\varphi-\left(\eta\frac{\partial}{\partial\xi}\right)_{f0}(j_\zeta)_{f0}\sin n\varphi\sin m\varphi\Big]$$

$$-\frac{e\hbar q}{m}(j_\xi)_{f0}\Big[\left(\eta\frac{\partial}{\partial\eta}\right)_{f0}-\left(\zeta\frac{\partial}{\partial\zeta}\right)_{f0}\Big](\sin m\varphi\cos m\varphi+\sin n\varphi\cos n\varphi)$$

$$+\frac{e\hbar q}{m}(j_\xi)_{f0}\Big[\left(\eta\frac{\partial}{\partial\zeta}\right)_{f0}(\sin^2 m\varphi+\sin^2 n\varphi)-\left(\zeta\frac{\partial}{\partial\eta}\right)_{f0}(\cos^2 m\varphi$$

$$+\cos^2 n\varphi)\Big]\Big\}G_{nm}(\omega). \qquad (6)$$

Taking $g(n\varphi)$ as a suitable function of $n\varphi$, several terms in the right hand side of (6) have the form

$$\sum_n\sum_m\Big[g(m\varphi)\pm g(n\varphi)\Big]G_{nm}(\omega).$$

On the other hand, $G_{nm}(\omega)$ is the function dependent only on $|n-m|$ as far as the boundary effect is neglected, namely,

$$G_{nm}(\omega)=G_{mn}(\omega)$$

holds, which is clear from the fact that the interaction is the function of its distance. Hence we obtain the relations

$$\sum_{n}\sum_{m}\Big[g(m\varphi)-g(n\varphi)\Big]G_{nm}(\omega)=0$$

and

$$\sum_{n}\sum_{m}\Big[g(m\varphi)+g(n\varphi)\Big]G_{nm}(\omega)=\frac{2}{N}\sum_{K}\sum_{n}\sum_{m}g(m\varphi)e^{-iK(n-m)}G_{K}(\omega),$$

where $G_K(\omega)$ is defined by

$$G_{nm}(\omega)=\frac{1}{N}\sum_{K}G_K(\omega)\exp[-iK(n-m)].$$

By dividing the summations on n and m into $\sum_{n}\sum_{n-m}$, it becomes

$$\frac{2}{N}\sum_{n}\sum_{m}g(m\varphi)e^{-iK(n-m)}G_K(\omega)=2G_{K=0}(\omega)\sum_{m}g(m\varphi).$$

If $g(m\varphi)$ is the periodic function of m, $\sum_{m}g(m\varphi)$ vanishes. The first, second and fourth terms in the curly bracket of (6) vanish by these reasons. When $g(m\varphi)=\sin^2 m\varphi$ or $\cos^2 m\varphi$, it leads to the relation

$$\sum_{m}g(m\varphi)=\frac{N}{2}.$$

One may finally obtain

$$Q(q,\omega)=-\frac{\pi h\omega N}{\Delta}\frac{ehq}{m}\left\{\left[(j_\eta)_{f0}\left(\zeta\frac{\partial}{\partial\xi}\right)_{f0}-(j_\zeta)_{f0}\left(\eta\frac{\partial}{\partial\xi}\right)_{f0}\right]G_{K=\varphi}(\omega)\right.$$
$$\left.+(j_\xi)_{f0}\left[\left(\eta\frac{\partial}{\partial\zeta}\right)_{f0}-\left(\zeta\frac{\partial}{\partial\eta}\right)_{f0}\right]G_{K=0}(\omega)\right\}. \qquad (7)$$

According to Moffitt[4], it is convenient to take the ζ-axis as the helical axis and its transformation is performed correctly by using ζ, ξ and η instead of ξ, η and ζ, that is,

$$Q(q,\omega)=-\frac{\pi h\omega N}{\Delta}\frac{ehq}{m}\left\{\left[(j_\xi)_{f0}\left(\eta\frac{\partial}{\partial\zeta}\right)_{f0}-(j_\eta)_{f0}\left(\xi\frac{\partial}{\partial\zeta}\right)_{f0}\right]G_{K=\varphi}(\omega)\right.$$
$$\left.+(j_\zeta)_{f0}\left[\left(\xi\frac{\partial}{\partial\eta}\right)_{f0}-\left(\eta\frac{\partial}{\partial\xi}\right)_{f0}\right]G_{K=0}(\omega)\right\}. \qquad (7')$$

Using the expression[1])

$$G_K(\omega) = \frac{2}{[\hbar\omega - (\Delta^2/\hbar\omega)] - 2(\Delta/\hbar\omega)V(K)} \tag{8}$$

and

$$V(K) = \sum_{n-m=0}^{N-1} V_{nm} e^{iK(n-m)}, \tag{9}$$

and the relation for the matrix elements between the current operator $\boldsymbol{j}$ and the dipole moment operator $\boldsymbol{\mu}$

$$(j_\eta)_{f0} = \frac{i\Delta}{\hbar}(\mu_\eta)_{f0},$$

we expand the (7) into the power series of V up to the linear term of V. Then, it is found that $Q(q, \omega)$ is proportional to q. Therefore, $\Delta q = q^- - q^+$ may finally be expressed as

$$\begin{aligned}\Delta q &= -\frac{i}{c^2}\frac{1}{q}Q(q, \omega)\\ &= \frac{2\pi N\hbar\omega e}{mc^2}\Big\{\frac{\hbar\omega}{(\hbar\omega)^2 - \Delta^2}\Big[\Big(\eta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\zeta)_{f0} - \Big(\zeta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\eta)_{f0} + \Big(\Big(\zeta\frac{\partial}{\partial\eta}\Big)_{f0} - \Big(\eta\frac{\partial}{\partial\zeta}\Big)_{f0}\Big)(\mu_\xi)_{f0}\Big]\\ &+ \frac{2\Delta\hbar\omega}{[(\hbar\omega)^2 - \Delta^2]^2}\Big(\Big[\sum_{n-m=0}^{N-1} V_{nm}\cos(n-m)\varphi\Big]\Big[\Big(\eta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\zeta)_{f0} - \Big(\zeta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\eta)_{f0}\Big]\\ &+ \Big[\sum_{n-m=0}^{N-1} V_{nm}\Big]\Big[\Big(\Big(\zeta\frac{\partial}{\partial\eta}\Big)_{f0} - \Big(\eta\frac{\partial}{\partial\zeta}\Big)_{f0}\Big)(\mu_\xi)_{f0}\Big]\Big)\Big\}.\end{aligned} \tag{10}$$

The similar results are obtained in comparison with those considered in the case of the incident wave parallel to the helical axis, namely, the first term in the curly bracket is the intrinsic rotation and the second term arises from the energy shift of the intrinsic chromophore due to the exciton. But the term relating to the splitting of the absorption of light does not appear. It should be noted that Δq is proportional to η or ζ, and so, the rotational strength contains explicitly the helical radius of the polymer in the present case.

§ 3. The optical rotation for the randomly oriented polymers

In the case of random arrangement of polymers to the light, the average optical rotation $\overline{\Delta q}$ is given by $(\Delta q_{//} + 2\Delta q_{\perp})/3$, where $\Delta q_{//}$ and $\Delta q_{\perp}$ are Δq for light incident parallel and perpendicular to the helical axis, respectively. Therefore, it can be concluded that $\overline{\Delta q}$ is expressed as

$$\overline{\Delta q} = \frac{4\pi N\hbar\omega e}{3mc^2}\Bigg\{\frac{\hbar\omega}{(\hbar\omega)^2-\Delta^2}\Bigg[3\Bigg(\Big(\zeta\frac{\partial}{\partial\eta}\Big)_{f0}(\mu_\xi)_{f0}-\Big(\zeta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\eta)_{f0}\Bigg)+\Big(\eta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\zeta)_{f0}-\Big(\eta\frac{\partial}{\partial\zeta}\Big)_{f0}(\mu_\xi)_{f0}\Bigg]$$

$$+\frac{2\Delta\hbar\omega}{[(\hbar\omega)^2-\Delta^2]^2}\Bigg(\Bigg[\sum_{n-m=0}^{N-1}V_{nm}\cos(n-m)\varphi\Bigg]\Bigg[\Big(\eta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\zeta)_{f0}+2\Big(\zeta\frac{\partial}{\partial\eta}\Big)_{f0}(\mu_\xi)_{f0}$$

$$-3\Big(\zeta\frac{\partial}{\partial\xi}\Big)_{f0}(\mu_\eta)_{f0}\Bigg]+\Bigg[\sum_{n-m=0}^{N-1}V_{nm}\Bigg]\Bigg[\Bigg(\Big(\zeta\frac{\partial}{\partial\eta}\Big)_{f0}-\Big(\eta\frac{\partial}{\partial\zeta}\Big)_{f0}\Bigg)(\mu_\xi)_{f0}\Bigg]\Bigg)$$

$$+\frac{md}{e\hbar^2}\frac{2\Delta^2\hbar\omega}{[(\hbar\omega)^2-\Delta^2]^2}\Bigg[\sum_{n-m=0}^{N-1}(n-m)V_{nm}\sin(n-m)\varphi\Bigg]\Bigg[(\mu_\xi)_{f0}(\mu_\xi)_{f0}+(\mu_\eta)_{f0}(\mu_\eta)_{f0}\Bigg]\Bigg\}, \tag{11}$$

and agrees with Moffitt, Fitts and Kirkwood's formula[5]. The third term in the curly bracket represents the so-called "anomalous dispersion" and the contribution from the splitting of the absorption of light only parallel to the helical axis.

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