Theory of Medium-Induced Optical Activities

F. C. Hsu[a,c] (許峰誠), Y.-T. Kuo[a] (郭于慈), Y.-J. Shiu[a,c] (許瑛珍),
K. K. Liang[a] (梁國淦), M. Hayashi[b] (林倫年),
T.-C. Chang[a] (張大釗) and S. H. Lin[a,c]* (林聖賢)
[a] *Institute of Atomic and Molecular Science, Academic Sinica, Taipei, Taiwan, R.O.C.*
[b] *Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan, R.O.C.*
[c] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*

In this paper, using the dipole-dipole interactions to describe the interaction between the system molecule and medium molecules, a theory of medium-induced optical activity has been developed. We have shown that the symmetry technique can be used to determine the types of electronic states that can be involved in the medium-induced optical activity and that the octant rule can be deduced by using our theory.

1. INTRODUCTION

The optical activity induced by interaction to DNA of dye molecules has attracted considerable attention.[1-10] This is mainly due to the fact that the induced optical activity can provide a sensitive spectroscopic probe for detecting intercalation mechanisms. Various theories have been proposed.[1-3,6-8] Crystallographic and NMR studies for drug (or dye)/oligonucleotide complexes provide structural information about binding sites, but for solution structures with longer DNA, spectroscopic studies can be much more revealing despite representing an average. By examining spectroscopically the interactions of a dye or a drug with polynucleotides of defined sequences under varying conditions, a model may be constructed of how the dye (or drug) molecule may interact in different ways with heterogeneous DNA.

The main purpose of this paper is to present a theory of the optical activity induced by optically active mediums. We assume that the dipole-dipole interactions between the system molecule and medium molecules are responsible for modifying the electronic wavefunctions of the system molecules. However, this can easily be generalized. We shall show that the symmetry argument can be used to determine the types of electronic states which can be involved in perturbing the electronic dipole transition moment or the electronic magnetic transition moment.

2. THEORY

According to the perturbation theory, to the first-order approximation the wavefunction can be expressed as

$$\varphi_n = \varphi_n^0 + \sum_m{}' \frac{H'_{mn}}{E_n^0 - E_m^0}\varphi_m^0 + \cdots \tag{2-1}$$

where $\hat{H}'$ denotes the perturbation. In our case, $\hat{H}'$ represents the interaction between the system molecule and medium (or bath) molecules. For optical activity, we are concerned with the rotational strength for, say, the electronic transition $g \to e$,[11,12]

$$R_{eg} = \mathrm{Im}\left(\vec{M}_{eg} \cdot \vec{\mu}_{ge}\right) \tag{2-2}$$

where $\vec{M}_{eg}$ and $\vec{\mu}_{ge}$ represent the matrix elements of electronic magnetic moment and electronic moment, respectively. That is,

$$\vec{M}_{eg} = \left\langle \varphi_e \middle| \vec{M} \middle| \varphi_g \right\rangle \tag{2-3}$$

and

$$\vec{\mu}_{ge} = \left\langle \varphi_g \middle| \vec{\mu} \middle| \varphi_e \right\rangle \tag{2-4}$$

Applying Eq. (2-1) to φ_g and φ_e in Eq. (2-2) yields

$$\varphi_g = \varphi_g^0 + \sum_{e'} \alpha_{e'g}\varphi_{e'}^0 + \cdots \tag{2-5}$$

and

$$\varphi_e = \varphi_e^0 + \sum_{e'} \alpha_{e'e}\varphi_{e'}^0 + \cdots \tag{2-6}$$

where for example, $\alpha_{e'g} = \dfrac{H'_{e'g}}{E_g^0 - E_{e'}^0}$. It follows that

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$$R_{eg} = \mathrm{Im}\Big[\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{ge}\big)+\sum_{e'}\alpha_{e'e}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{ge'}\big)+\sum_{e'}\alpha^*_{e'g}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e'e}\big)+$$
$$\sum_{e'}\alpha_{e'g}\big(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{ge}\big)+\sum_{e'}\alpha^*_{e'e}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge}\big)+\sum_{e'}\sum_{e''}\Big\{\alpha^*_{e''g}\alpha_{e'e}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\big)+$$
$$\alpha^*_{e'e}\alpha_{e''e}\big(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\big)+\alpha_{e''g}\alpha_{e'e}\big(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\big)+\alpha^*_{e'e}\alpha_{e''e}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\big)+$$
$$\alpha^*_{e'e}\alpha^*_{e''g}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\big)\Big\}+\sum_{e'}\sum_{e''}\alpha_{e''g}\alpha^*_{e''g}\big(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\big)+\cdots\Big] \qquad (2\text{-}7)$$

For medium-induced optical activity (MIOA), the term ($\vec{M}^0_{eg}\cdot\vec{\mu}^0_{ge}$) vanishes.

Next we shall apply the group theory to treat MIOA. For this purpose, we shall consider the case in which the molecule has the C_{2v} symmetry. The following cases will be considered.

(1) Case 1: A_1 ground state and A_2 excited state.

This case corresponds to the $n\rightarrow\pi^*$ transition of the carbonyl compound like formaldehyde, acetone, etc. In the approximation of dipole-dipole interactions for $\hat{H}'$, we find

$$\alpha_{e'e}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{ge'}\big)=0 \qquad (2\text{-}8)$$

and

$$\alpha^*_{e'g}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e'e}\big)=0 \qquad (2\text{-}9)$$

where for example

$$\alpha_{e'e}=\sum_m\frac{1}{\varepsilon R_m^3}\left[\vec{\mu}_{e'e}\cdot\vec{\mu}_m-\frac{3\big(\vec{\mu}_{e'e}\cdot\vec{R}_m\big)\big(\vec{\mu}_m\cdot\vec{R}_m\big)}{R_m^2}\right]. \qquad (2\text{-}10)$$

Here $\vec{\mu}_{e'e}$ denotes the transition moment of the system molecule, while $\vec{\mu}_m$ represents the dipole moment of the m-th bath molecules with the distance R_m between the two molecules. The symmetry argument can be used to determine whether $\alpha_{e'e}$ vanishes or not through $\vec{\mu}_{e'e}$.

Since $\vec{\mu}^0_{ge}=0$ for $A_1\rightarrow A_2$, Eq. (2-7) reduces to

$$R_{eg}=\mathrm{Im}\Big[\sum_{e'}\sum_{e''}\alpha_{e'g}\alpha^*_{e''g}\big(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\big)+\sum_{e'}\sum_{e''}\Big\{\alpha^*_{e''g}\alpha_{e'e}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\big)+$$
$$\alpha_{e''g}\alpha_{e'e}\big(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\big)+\alpha^*_{e'e}\alpha_{e''e}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\big)+$$
$$\alpha^*_{e'e}\alpha^*_{e''g}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\big)\Big\}+\cdots\Big]. \qquad (2\text{-}11)$$

or

$$R_{eg}=\sum_{i=1}^{5}R_{eg}^{(i)} \qquad (2\text{-}12)$$

where for example,

$$R_{eg}^{(1)}=\sum_{e'}\sum_{e''}\mathrm{Im}\Big[\alpha_{e'g}\alpha^*_{e''g}\big(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\big)\Big]. \qquad (2\text{-}13)$$

For $R_{eg}^{(1)}$, using the symmetry arguments we obtain

$$R_{eg}^{(1)}=\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\Big[\alpha_{e'g}\alpha^*_{e''g}\big\langle\varphi^0_e\big|\hat{M}_x\big|\varphi^0_{e'}\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_x\big|\varphi^0_e\big\rangle\Big]+$$
$$\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\Big[\alpha_{e'g}\alpha^*_{e''g}\big\langle\varphi^0_e\big|\hat{M}_y\big|\varphi^0_{e'}\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_y\big|\varphi^0_e\big\rangle\Big] \qquad (2\text{-}14)$$

Similarly for $R_{eg}^{(2)}$,

$$R_{eg}^{(2)}=\sum_{e'}\sum_{e''}\mathrm{Im}\Big[\alpha^*_{e''g}\alpha_{e'e}\big(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\big)\Big] \qquad (2\text{-}15)$$

we obtain

$$R_{eg}^{(2)}=\sum_{e''\in B_1}\sum_{e'\in B_1}\mathrm{Im}\Big[\alpha^*_{e''g}\alpha_{e'e}\big\langle\varphi^0_e\big|\hat{M}_z\big|\varphi^0_g\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_z\big|\varphi^0_{e'}\big\rangle\Big]+$$
$$\sum_{e''\in B_2}\sum_{e'\in B_2}\mathrm{Im}\Big[\alpha^*_{e''g}\alpha_{e'e}\big\langle\varphi^0_e\big|\hat{M}_z\big|\varphi^0_g\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_z\big|\varphi^0_{e'}\big\rangle\Big] \qquad (2\text{-}16)$$

for $R_{eg}^{(3)}$

$$R_{eg}^{(3)}=\sum_{e'}\sum_{e''}\mathrm{Im}\Big[\alpha_{e''g}\alpha_{e'e}\big(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\big)\Big]$$
$$=\sum_{e''\in B_1}\sum_{e'\in B_1}\mathrm{Im}\Big[\alpha_{e''g}\alpha_{e'e}\big\langle\varphi^0_e\big|\hat{M}_x\big|\varphi^0_{e''}\big\rangle\big\langle\varphi^0_g\big|\hat{\mu}_x\big|\varphi^0_{e'}\big\rangle\Big]+$$
$$\sum_{e''\in B_2}\sum_{e'\in B_2}\mathrm{Im}\Big[\alpha_{e''g}\alpha_{e'e}\big\langle\varphi^0_e\big|\hat{M}_y\big|\varphi^0_{e''}\big\rangle\big\langle\varphi^0_g\big|\hat{\mu}_y\big|\varphi^0_{e'}\big\rangle\Big] \qquad (2\text{-}17)$$

for $R_{eg}^{(4)}$

$$R_{eg}^{(4)}=\sum_{e'}\sum_{e''}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha_{e''e}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\big)\Big]$$
$$=\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha_{e''e}\big\langle\varphi^0_{e'}\big|\hat{M}_y\big|\varphi^0_g\big\rangle\big\langle\varphi^0_g\big|\hat{\mu}_y\big|\varphi^0_{e''}\big\rangle\Big]+$$
$$\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha_{e''e}\big\langle\varphi^0_{e'}\big|\hat{M}_x\big|\varphi^0_g\big\rangle\big\langle\varphi^0_g\big|\hat{\mu}_x\big|\varphi^0_{e''}\big\rangle\Big] \qquad (2\text{-}18)$$

and for $R_{eg}^{(5)}$

$$R_{eg}^{(5)}=\sum_{e'}\sum_{e''}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha_{e''g}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\big)\Big]$$
$$=\sum_{e'\in B_1}\sum_{e''\in B_1}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha^*_{e''g}\big\langle\varphi^0_{e'}\big|\hat{M}_y\big|\varphi^0_g\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_y\big|\varphi^0_e\big\rangle\Big]+$$
$$\sum_{e'\in B_2}\sum_{e''\in B_2}\mathrm{Im}\Big[\alpha^*_{e'e}\alpha^*_{e''g}\big\langle\varphi^0_{e'}\big|\hat{M}_x\big|\varphi^0_g\big\rangle\big\langle\varphi^0_{e''}\big|\hat{\mu}_x\big|\varphi^0_e\big\rangle\Big]. \qquad (2\text{-}19)$$

(2) Case 2: A_1 ground state and A_1 excited state

In this case we find

$$R_{eg}=\mathrm{Im}\Big[\sum_{e'}\sum_{e''}\Big\{\alpha_{e''g}\alpha_{e'e}\big(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\big)+\alpha^*_{e'e}\alpha_{e''e}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\big)+$$
$$\alpha^*_{e'e}\alpha^*_{e''g}\big(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\big)\Big\}+\sum_{e'}\sum_{e''}\alpha_{e'g}\alpha^*_{e''e}\big(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\big)+$$

$$\sum_{e'}\sum_{e''}\left\{\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\right)\right\}+\cdots\Big]=\sum_{i=1}^{5}R^{(i)}_{eg} \tag{2-20}$$

where

$$R_{eg}^{(1)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\right)\right]=$$

$$\sum_{e''\in B_2}\sum_{e'\in B_1}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_{e'}\right\rangle\right]+$$

$$\sum_{e''\in B_1}\sum_{e'\in B_2}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle\right] \tag{2-21}$$

$$R_{eg}^{(2)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\right)\right]=$$

$$\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_y\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_{e''}\right\rangle\right]+$$

$$\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_x\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e''}\right\rangle\right] \tag{2-22}$$

$$R_{eg}^{(3)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\right)\right]=$$

$$\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left\langle\varphi^0_{e'}\middle|\hat{M}_y\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_y\middle|\varphi^0_e\right\rangle\right]+$$

$$\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left\langle\varphi^0_{e'}\middle|\hat{M}_x\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_x\middle|\varphi^0_e\right\rangle\right] \tag{2-23}$$

$$R_{eg}^{(4)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\right)\right]=$$

$$\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_y\middle|\varphi^0_e\right\rangle\right]+$$

$$\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_x\middle|\varphi^0_e\right\rangle\right] \tag{2-24}$$

and

$$R_{eg}^{(5)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\right)\right]$$

$$=\sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\left\{\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_z\middle|\varphi^0_{e''}\right\rangle+\alpha^*_{e''e}\alpha_{e'e}\left\langle\varphi^0_{e''}\middle|\hat{M}_z\middle|\varphi^0_{e'}\right\rangle\right\}\times\right.$$

$$\left.\left\langle\varphi^0_g\middle|\hat{\mu}_z\middle|\varphi^0_e\right\rangle\right] \tag{2-24A}$$

(3)Case 3: A_1 ground state and B_1 excited state.

No tice that in this case we have

$$R_{eg}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\right)+\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\right)+\right.$$

$$\alpha_{e''g}\alpha_{e'e}\left(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\right)+\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\right)+$$

$$\left.\alpha^*_{e'e}\alpha^*_{e''g}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\right)\right]+\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\right)\right]+\cdots$$

$$=\sum_{i=1}^{6}R^{(i)}_{eg} \tag{2-25}$$

where

$$R_{eg}^{(1)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\right)\right]$$

$$=\sum_{e'\in A_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e'g}\alpha_{e''e}\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_y\middle|\varphi^0_{e'}\right\rangle\right]$$

$$+\sum_{e'\in A_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_y\middle|\varphi^0_{e'}\right\rangle\right] \tag{2-26}$$

$$R_{eg}^{(2)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\right)\right]$$

$$=\sum_{e'\in A_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_x\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_e\right\rangle\right] \tag{2-27}$$

$$R_{eg}^{(3)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\right)\right]$$

$$=\sum_{e'\in A_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_z\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_z\middle|\varphi^0_{e'}\right\rangle\right] \tag{2-28}$$

$$R_{eg}^{(4)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\right)\right]$$

$$=\sum_{e'\in A_2}\sum_{e''\in A_1}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_z\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_z\middle|\varphi^0_{e''}\right\rangle\right] \tag{2-29}$$

$$R_{eg}^{(5)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\right)\right]$$

$$=\sum_{e'\in A_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left\langle\varphi^0_{e'}\middle|\hat{M}_z\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_z\middle|\varphi^0_e\right\rangle\right] \tag{2-30}$$

$$R_{eg}^{(6)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\right)\right]$$

$$=\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left\langle\varphi^0_e\middle|\hat{M}_z\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_z\middle|\varphi^0_e\right\rangle\right] \tag{2-31}$$

(4)Case 4: A_1 ground state and B_2 excited state.

As in the case of Case 3, we have

$$R_{eg}=\sum_{i=1}^{6}R_{eg}^{(i)} \tag{2-32}$$

where

$$R_{eg}^{(1)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left(\vec{M}^0_{eg}\cdot\vec{\mu}^0_{e''e'}\right)\right]$$

$$=\sum_{e'\in A_2}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_e\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle\right]$$

$$+\sum_{e'\in A_1}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha^*_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle\right] \tag{2-33}$$

$$R_{eg}^{(2)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'e''}\cdot\vec{\mu}^0_{ge}\right)\right]$$

$$=\mathrm{Im}\left[\left\{\sum_{e'\in A_2}\sum_{e''\in B_2}\left\langle\varphi^0_{e'}\middle|\hat{M}_y\middle|\varphi^0_{e''}\right\rangle+\sum_{e'\in B_2}\sum_{e''\in A_2}\left\langle\varphi^0_{e'}\middle|\hat{M}_y\middle|\varphi^0_{e''}\right\rangle\right\}\times\right.$$

$$\left.\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_e\right\rangle\right] \tag{2-34}$$

$$R_{eg}^{(3)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left(\vec{M}^0_{ee''}\cdot\vec{\mu}^0_{ge'}\right)\right]$$

$$=\sum_{e'\in A_1}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e''g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_z\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_z\middle|\varphi^0_{e'}\right\rangle\right] \tag{2-35}$$

$$R_{eg}^{(4)}=\sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{ge''}\right)\right]$$

$$= \sum_{e'\in A_2}\sum_{e''\in A_1} \mathrm{Im}\left[\alpha^*_{e'e}\alpha_{e''e}\left\langle\varphi^0_{e'}\middle|\hat{M}_z\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_z\middle|\varphi^0_{e''}\right\rangle\right] \quad (2\text{-}36)$$

$$R_{eg}^{(5)} = \sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left(\vec{M}^0_{e'g}\cdot\vec{\mu}^0_{e''e}\right)\right]$$

$$= \sum_{e'\in A_2}\sum_{e''\in B_2} \mathrm{Im}\left[\alpha^*_{e'e}\alpha^*_{e''g}\left\langle\varphi^0_{e'}\middle|\hat{M}_z\middle|\varphi^0_g\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_z\middle|\varphi^0_e\right\rangle\right] \quad (2\text{-}37)$$

and

$$R_{eg}^{(6)} = \sum_{e'}\sum_{e''}\mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left(\vec{M}^0_{ee'}\cdot\vec{\mu}^0_{e''e}\right)\right]$$

$$= \sum_{e'\in B_1}\sum_{e''\in B_2} \mathrm{Im}\left[\alpha_{e'g}\alpha^*_{e''g}\left\langle\varphi^0_e\middle|\hat{M}_z\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_{e''}\middle|\hat{\mu}_z\middle|\varphi^0_e\right\rangle\right] \quad (2\text{-}38)$$

3. APPLICATIONS TO $A_1 \to A_1$ OF THE C_{2V} MOLECULE

To show the application of the theoretical results presented in the previous section, we consider the case of $A_1 \to A_1$, in particular, $\sigma \to \sigma^*$. Notice that

$$\varphi_g = \left|\overset{+}{x}_\sigma\,\overset{-}{x}_\sigma\,\overset{+}{x}_{\pi x}\,\overset{-}{x}_{\pi x}\,\overset{+}{x}_{\pi y}\,\overset{-}{x}_{\pi y}\right| \quad (3\text{-}1)$$

$$\varphi_e = \frac{1}{\sqrt{2}}\left(\left|\overset{+}{x}_{\sigma^*}\,\overset{-}{x}_\sigma\,\overset{+}{x}_{\pi x}\,\overset{-}{x}_{\pi x}\,\overset{+}{x}_{\pi y}\,\overset{-}{x}_{\pi y}\right| - \left|\overset{-}{x}_{\sigma^*}\,\overset{+}{x}_\sigma\,\overset{+}{x}_{\pi x}\,\overset{-}{x}_{\pi x}\,\overset{+}{x}_{\pi y}\,\overset{-}{x}_{\pi y}\right|\right) \quad (3\text{-}2)$$

and that similar expressions can be obtained for $\varphi_{e'}(\sigma \to \pi_x^*)$ and $\varphi_{e''}(\sigma \to \pi_y^*)$. Using these wavefunctions, we can calculate the matrix elements of dipole moment and magnetic moment, e.g.,

$$\left\langle\varphi_e\middle|\hat{\mu}_x\middle|\varphi_{e'}\right\rangle = \left\langle x_{\sigma^*}\middle|\hat{\mu}_x(1)\middle|x_{\pi_x^*}\right\rangle \quad (3\text{-}3)$$

$$\left\langle\varphi_e\middle|\hat{\mu}_z\middle|\varphi_g\right\rangle = \sqrt{2}\left\langle x_{\sigma^*}\middle|\hat{\mu}_z(1)\middle|x_\sigma\right\rangle \quad (3\text{-}4)$$

etc. where $\hat{\mu}_x(1)$ and $\hat{\mu}_z(1)$ denote the one-electron operators. For simplicity, we shall employ the simple molecular orbitals,

$$x_\sigma = C_1\chi_s(1) + C_2\chi_s(2) \quad (3\text{-}5)$$

$$x_{\sigma^*} = C_1'\chi_s(1) + C_2'\chi_s(2) \quad (3\text{-}6)$$

$$x_{\pi_x^*} = C_1''\chi_{px}(1) + C_2''\chi_{px}(2) \quad (3\text{-}7)$$

$$x_{\pi_y^*} = C_1''\chi_{py}(1) + C_2''\chi_{py}(2), \quad (3\text{-}8)$$

etc. In other words, for simplicity of demonstration we assume that the chromophore is a diatomic group (e.g., C=O).

(A) $R_{eg}^{(1)}$

Using the notations used in this section, we have

$$R_{eg}^{(1)} = \sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left\{\left[\alpha_{e'g}\alpha_{e'e}\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle\right] + \left[\alpha_{e''g}\alpha_{e''e}\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_{e''}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_{e''}\right\rangle\right]\right\} \quad (3\text{-}9)$$

where

$$\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle = \sqrt{2}\left\langle x_\sigma\middle|\hat{\mu}_z(1)\middle|x_{\pi_x^*}\right\rangle \quad (3\text{-}10)$$

$$\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_{e''}\right\rangle = \sqrt{2}\left\langle x_\sigma\middle|\hat{\mu}_y(1)\middle|x_{\pi_y^*}\right\rangle \quad (3\text{-}11)$$

$$\left\langle\varphi^0_e\middle|\hat{\mu}_y\middle|\varphi^0_{e''}\right\rangle = \left\langle x_{\sigma^*}\middle|\hat{M}_y(1)\middle|x_{\pi_x^*}\right\rangle \quad (3\text{-}12)$$

and

$$\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e'}\right\rangle = \left\langle x_{\sigma^*}\middle|\hat{M}_x(1)\middle|x_{\pi_y^*}\right\rangle \quad (3\text{-}13)$$

For simplicity we shall use the atomic orbitals,

$$\chi_s = N_s r e^{-\alpha r} \quad (3\text{-}14)$$

$$\chi_{px} = N_p x e^{-\alpha r} \quad (3\text{-}15)$$

$$\chi_{py} = N_p y e^{-\alpha r} \quad (3\text{-}16)$$

where $N_s = \left(\frac{\alpha^5}{3\pi}\right)^{\frac{1}{2}}$ and $N_p = \left(\frac{\alpha^5}{\pi}\right)^{\frac{1}{2}}$. In the one-center approximation, we find

$$\left\langle\varphi^0_g\middle|\hat{\mu}_y\middle|\varphi^0_{e''}\right\rangle = \left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle = \frac{5e}{\alpha\sqrt{6}}\left(C_1C_1'' + C_2C_2''\right) \quad (3\text{-}17)$$

and

$$\left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e'}\right\rangle = \frac{(\alpha R)}{4\sqrt{3}}\left(\frac{\gamma h}{2\pi i}\right)\left(C_1'C_1'' - C_2'C_2''\right) = -\left\langle\varphi^0_e\middle|\hat{M}_y\middle|\varphi^0_{e''}\right\rangle \quad (3\text{-}18)$$

where $\gamma = \frac{e}{2mc}$ and R denotes the internuclear distance. It follows that

$$R_{eg}^{(1)} = \sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\left(\alpha_{e''g}\alpha_{e''e} - \alpha_{e'g}\alpha_{e'e}\right)\times \left\langle\varphi^0_e\middle|\hat{M}_x\middle|\varphi^0_{e'}\right\rangle\left\langle\varphi^0_g\middle|\hat{\mu}_x\middle|\varphi^0_{e'}\right\rangle\right] \quad (3\text{-}19)$$

or

$$R_{eg}^{(1)} = \sum_{e'\in B_1}\sum_{e''\in B_2}\mathrm{Im}\left[\left(\alpha_{e''g}\alpha_{e''e} - \alpha_{e'g}\alpha_{e'e}\right)\times \left(C_1C_1'' + C_2C_2''\right)\left(C_1'C_1'' - C_2'C_2''\right)\frac{(5eR)}{12\sqrt{2}}\left(\frac{\gamma h}{2\pi i}\right)\right] \quad (3\text{-}20)$$

(B) $R_{eg}^{(1)}$

Notice that

$$R_{eg}^{(2)} = \sum_{e'\in B_1}\sum_{e''\in B_2} \mathrm{Im}\Big[\alpha^*_{e'e}\alpha_{e''e}\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle\langle\varphi^0_g|\hat{\mu}_y|\varphi^0_{e''}\rangle + \alpha^*_{e''e}\alpha_{e'e}\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle\langle\varphi^0_g|\hat{\mu}_x|\varphi^0_{e'}\rangle\Big] \tag{3-21}$$

where

$$\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle = \sqrt{2}\,\langle x_{\pi_x^*}|\hat{M}_y(1)|x_\sigma\rangle \tag{3-22}$$

$$\langle\varphi^0_g|\hat{\mu}_y|\varphi^0_{e''}\rangle = \sqrt{2}\,\langle x_\sigma|\hat{\mu}_y(1)|x_{\pi_y^*}\rangle \tag{3-23}$$

$$\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle = \sqrt{2}\,\langle x_{\pi_y^*}|\hat{M}_x(1)|x_\sigma\rangle \tag{3-24}$$

and

$$\langle\varphi^0_g|\hat{\mu}_x|\varphi^0_{e'}\rangle = \sqrt{2}\,\langle x_\sigma|\hat{\mu}_x(1)|x_{\pi_x^*}\rangle \tag{3-25}$$

It follows that

$$\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle = \sqrt{2}\Big(C_1C_1^{\prime *}\langle x_{px}(1)|\hat{M}_y(1)|x_s(1)\rangle + C_2C_2^{\prime *}\langle x_{px}(2)|\hat{M}_y(1)|x_s(2)\rangle\Big) \tag{3-26}$$

$$\langle\varphi^0_g|\hat{\mu}_y|\varphi^0_{e''}\rangle = \sqrt{2}\Big(C_1C^{\prime *}\langle x_s(1)|\hat{\mu}_y(1)|x_{py}(1)\rangle + C_2C_2^{\prime\prime *}\langle x_s(2)|\hat{\mu}_y(2)|x_{py}(2)\rangle\Big) \tag{3-27}$$

$$\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle = \sqrt{2}\Big(C_1C_1^{\prime\prime *}\langle x_{py}(1)|\hat{M}_x(1)|x_s(1)\rangle + C_2C_2^{\prime\prime *}\langle x_{py}(2)|\hat{M}_x(1)|x_s(2)\rangle\Big) \tag{3-28}$$

and

$$\langle\varphi^0_g|\hat{\mu}_x|\varphi^0_{e'}\rangle = \sqrt{2}\Big(C_1C_1^{\prime *}\langle x_s(1)|\hat{\mu}_x(1)|x_{px}(1)\rangle + C_2C_2^{\prime\prime *}\langle x_s(2)|\hat{\mu}_x(1)|x_{px}(2)\rangle\Big) \tag{3-29}$$

where

$$\langle x_{px}(1)|\hat{M}_y(1)|x_s(1)\rangle = \frac{\gamma h}{2\pi i}\left\langle x_{px}(1)\left|z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right|x_s(1)\right\rangle$$

$$= \langle x_s(1)|\hat{M}_y(1)|x_{px}(1)\rangle^* = -\frac{\gamma h}{2\pi i}\left\langle x_s(1)\left|z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right|x_{px}(1)\right\rangle$$

$$= \left(\frac{\gamma h}{2\pi i}\right)\frac{(\alpha R)}{4\sqrt{3}} \tag{3-30}$$

$$\langle x_{px}(2)|\hat{M}_y(1)|x_s(2)\rangle = \left(-\frac{\gamma h}{2\pi i}\right)\frac{(\alpha R)}{4\sqrt{3}} \tag{3-31}$$

$$\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle = \left(\frac{\gamma h}{2\pi i}\right)\frac{(\alpha R)}{2\sqrt{6}}\left(C_1C_1^{\prime *} - C_2C_2^{\prime\prime *}\right) = -\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle \tag{3-32}$$

$$\langle\varphi^0_g|\hat{\mu}_y|\varphi^0_{e''}\rangle = \frac{5e}{\sqrt{6}\alpha}\left(C_1C_1^{\prime\prime *} + C_2C_2^{\prime\prime *}\right) = \langle\varphi^0_g|\hat{\mu}_x|\varphi^0_{e'}\rangle \tag{3-33}$$

and

$$R_{eg}^{(2)} = 0 \tag{3-34}$$

if $\alpha_{e'e}$ and $\alpha_{e''e}$ are real.

(C) $R_{eg}^{(3)}$

Notice that

$$R_{eg}^{(3)} = \sum_{e'\in B_1}\sum_{e''\in B_2} \mathrm{Im}\Big[\alpha^*_{e'e}\alpha^*_{e''g}\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle\langle\varphi^0_{e''}|\hat{\mu}_y|\varphi^0_e\rangle + \alpha^*_{e''e}\alpha^*_{e'g}\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle\langle\varphi^0_{e'}|\hat{\mu}_x|\varphi^0_e\rangle\Big] \tag{3-35}$$

$$\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle = \sqrt{2}\,\langle x_{\pi_x^*}|\hat{M}_y(1)|x_\sigma\rangle \tag{3-36}$$

$$\langle\varphi^0_{e''}|\hat{M}_x|\varphi^0_g\rangle = \sqrt{2}\,\langle x_{\pi_y^*}|\hat{M}_x(1)|x_\sigma\rangle \tag{3-37}$$

$$\langle\varphi^0_{e''}|\hat{\mu}_y|\varphi^0_e\rangle = \langle x_{\pi_y^*}|\hat{\mu}_y(1)|x_{\sigma^*}\rangle \tag{3-38}$$

and

$$\langle\varphi^0_{e'}|\hat{\mu}_x|\varphi^0_e\rangle = \langle x_{\pi_x^*}|\hat{\mu}_x(1)|x_{\sigma^*}\rangle \tag{3-39}$$

It follows that

$$R_{eg}^{(3)} = \sum_{e'\in B_1}\sum_{e''\in B_2} \mathrm{Im}\Big[\left(\alpha^*_{e'e}\alpha^*_{e''g} - \alpha^*_{e''e}\alpha^*_{e'g}\right)\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle\langle\varphi^0_{e''}|\hat{\mu}_y|\varphi^0_e\rangle\Big] \tag{3-40}$$

where

$$\langle\varphi^0_{e''}|\hat{\mu}_y|\varphi^0_e\rangle = \frac{5e}{2\sqrt{3}\alpha}\left(C_1^{\prime}C_1^{\prime\prime *} + C_2^{\prime}C_2^{\prime\prime *}\right) \tag{3-41}$$

and $\langle\varphi^0_{e'}|\hat{M}_y|\varphi^0_g\rangle$ is given by Eq. (3-32).

(D) $R_{eg}^{(4)}$

Notice that

$$R_{eg}^{(4)} = \sum_{e' \in B_1} \sum_{e'' \in B_2} \mathrm{Im}\Big[\alpha_{e'g}\alpha^*_{e''g} \langle \varphi_e^0 | \hat{M}_y | \varphi_{e'}^0 \rangle \langle \varphi_{e''}^0 | \hat{\mu}_y | \varphi_e^0 \rangle + \alpha_{e''g}\alpha^*_{e'g} \langle \varphi_e^0 | \hat{M}_x | \varphi_{e''}^0 \rangle \langle \varphi_{e'}^0 | \hat{\mu}_x | \varphi_e^0 \rangle \Big] \quad (3\text{-}42)$$

$$\langle \varphi_{e'}^0 | \hat{\mu}_x | \varphi_e^0 \rangle = \langle x_{\pi_x^*} | \hat{\mu}_x(1) | x_{\sigma^*} \rangle \quad (3\text{-}43)$$

and

$$\langle \varphi_{e''}^0 | \hat{\mu}_y | \varphi_e^0 \rangle = \langle x_{\pi_y^*} | \hat{\mu}_y(1) | x_{\sigma^*} \rangle \quad (3\text{-}44)$$

or

$$\langle \varphi_{e'}^0 | \hat{\mu}_x | \varphi_e^0 \rangle = \langle \varphi_{e''}^0 | \hat{\mu}_y | \varphi_e^0 \rangle = \frac{5e}{2\sqrt{3}\alpha}\left(C_1'C_1'' + C_2'C_2''\right) \quad (3\text{-}45)$$

It follows that

$$R_{eg}^{(4)} = \sum_{e' \in B_1} \sum_{e'' \in B_2} \mathrm{Im}\Big[\left(\alpha_{e'g}\alpha^*_{e''g} - \alpha_{e''g}\alpha^*_{e'g}\right) \langle \varphi_e^0 | \hat{M}_y | \varphi_{e'}^0 \rangle \langle \varphi_{e''}^0 | \hat{\mu}_y | \varphi_e^0 \rangle \Big] \quad (3\text{-}46)$$

or

$$R_{eg}^{(4)} = 0 \quad (3\text{-}47)$$

if $\alpha_{e'g}$ and $\alpha_{e''g}$ are real.

(E) $R_{eg}^{(5)}$

Notice that

$$R_{eg}^{(5)} = \sum_{e' \in B_1} \sum_{e'' \in B_2} \mathrm{Im}\Big[\Big\{\alpha^*_{e'e}\alpha_{e''e} \langle \varphi_{e'}^0 | \hat{M}_z | \varphi_{e''}^0 \rangle + \alpha^*_{e''e}\alpha_{e'e} \langle \varphi_{e''}^0 | \hat{M}_z | \varphi_{e'}^0 \rangle \Big\} \langle \varphi_g^0 | \hat{\mu}_z | \varphi_e^0 \rangle \Big] \quad (3\text{-}48)$$

and since

$$\langle \varphi_{e''}^0 | \hat{M}_z | \varphi_{e'}^0 \rangle = \langle \varphi_{e'}^0 | \hat{M}_z | \varphi_{e''}^0 \rangle^* = -\langle \varphi_{e'}^0 | \hat{M}_z | \varphi_{e''}^0 \rangle \quad (3\text{-}49)$$

$$R_{eg}^{(5)} = 0 \quad (3\text{-}50)$$

if $\alpha_{e'e}$ and $\alpha_{e''e}$ are real.

In summary, for $A_1 \rightarrow A_1$ we obtain

$$R_{eg} = R_{eg}^{(1)} + R_{eg}^{(3)} \quad (3\text{-}51)$$

where $R_{eg}^{(1)}$ and $R_{eg}^{(3)}$ are given in Eq. (3-20) and Eq. (3-40), respectively.

4. DISCUSSION

In the previous sections, we have employed the perturbation method to treat the modification of the system electronic wavefunctions induced by the interaction with bath molecules. For the interaction between the system molecule and bath molecules, we assume that it is of the dipole-dipole interaction. To demonstrate how to evaluate the medium-induced optical rotational strength, we have used the chromophore of C_{2v} symmetry as an example and shown how to use the symmetry argument for this purpose. In Fig. 1, a demonstration of medium induced circular dichroism is shown. A dye molecule of C_{2v} symmetry, thionine, is shown here to be optically active (dash line) within the absorption region (solid line) when it is intercalated into the DNA sequence, say here, GC, whereas CD signals are never found in the absence of optically active medium.[13,14]

Next we shall show that the optical rotational strengths of $A_1 \rightarrow B_1$ and $A_1 \rightarrow B_2$ have the opposite signs. For simplicity we shall assume that the A_2 contributions can be neglected.

(A) $A_1 \rightarrow B_1$

Notice that

$$\langle \varphi_e^0 | \hat{M}_y | \varphi_g^0 \rangle = \sqrt{2}\Big(C_1C_1'' \langle x_{px}(1) | \hat{M}_y(1) | x_s(1) \rangle + C_2C_2'' \langle x_{px}(2) | \hat{M}_y(1) | x_s(2) \rangle \Big) \quad (4\text{-}1)$$

$$\langle \varphi_{e''}^0 | \hat{\mu}_y | \varphi_{e''}^0 \rangle = C_1'C_1'' \langle x_{px}(1) | \bar{\mu}_y(1) | x_s(1) \rangle + C_2'C_2'' \langle x_{py}(2) | \bar{\mu}_y(1) | x_s(2) \rangle \quad (4\text{-}2)$$

and that

$$\langle \pi_y(1) | \hat{\mu}_y(1) | x_s(1) \rangle = \langle \pi_y(2) | \hat{\mu}_y(1) | x_s(2) \rangle = \frac{5e}{2\sqrt{3}\alpha} \quad (4\text{-}3)$$

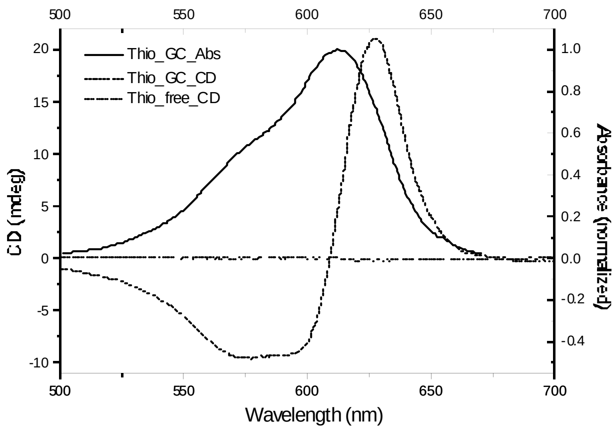

Fig. 1. Circular dichroism spectra of free thionine (dotted line) and thionine intercalated into GC (dashed line). Absorption spectrum of thionine in GC (solid line) is also shown here for comparison.

$$\left\langle x_{px}(1)\middle|\hat{M}_y(1)\middle|x_s(1)\right\rangle=\left(\frac{\gamma h}{2\pi i}\right)\frac{(\alpha R)}{4\sqrt{3}}=-\left\langle x_{px}(2)\middle|\hat{M}_y(1)\middle|x_s(2)\right\rangle \quad (4\text{-}4)$$

$$\left\langle \varphi_e^0\middle|\hat{M}_y\middle|\varphi_g^0\right\rangle=\sqrt{2}\left(C_1C_1''-C_2C_2'\right)\left(\frac{\gamma h}{2\pi i}\right)\frac{(\alpha R)}{4\sqrt{3}} \quad (4\text{-}5)$$

and

$$\left\langle \varphi_{e'}^0\middle|\hat{\mu}_y\middle|\varphi_{e''}^0\right\rangle=\left(C_1'C_1'+C_2'C_2'\right)\frac{5e}{2\sqrt{3}\alpha} \quad (4\text{-}6)$$

It follows that

$$R_{eg}^{(1)}=\sum_{e'\in A_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha_{e'g}^*\alpha_{e''e'}\sqrt{2}\left(C_1C_1'-C_2C_2'\right)\left(C_1'C_1'+C_2'C_2''\right)\times\left(\frac{\gamma h}{2\pi i}\right)\left(\frac{5eR}{24}\right)\right] \quad (4\text{-}7)$$

and that

$$R_{eg}^{(2)}=0,\ R_{eg}^{(4)}=0,\ R_{eg}^{(5)}=0 \quad (4\text{-}8)$$

Next we consider $R_{\mathrm{eg}}^{(3)}$

$$\left\langle \varphi_e^0\middle|\hat{M}_z\middle|\varphi_{e'}^0\right\rangle=\left\langle \pi_x^*\middle|\hat{M}_z(1)\middle|\pi_y^*\right\rangle=\left(C_1'^2\left\langle \chi_{px}(1)\middle|\hat{M}_z(1)\middle|\chi_{py}(1)\right\rangle+C_2'^2\left\langle \chi_{px}(2)\middle|\hat{M}_z(1)\middle|\chi_{py}(2)\right\rangle\right) \quad (4\text{-}9)$$

$$\left\langle \varphi_g^0\middle|\hat{\mu}_z\middle|\varphi_{e'}^0\right\rangle=\sqrt{2}\left\langle \sigma\middle|\hat{\mu}_z(1)\middle|\sigma^*\right\rangle=\sqrt{2}\left(C_1C_1'\left\langle \chi_s(1)\middle|\hat{\mu}_z(1)\middle|\chi_s(1)\right\rangle+C_2C_2'\left\langle \chi_s(2)\middle|\hat{\mu}_z(1)\middle|\chi_s(2)\right\rangle\right) \quad (4\text{-}10)$$

or

$$\left\langle \varphi_g^0\middle|\hat{\mu}_z\middle|\varphi_{e'}^0\right\rangle=\sqrt{2}\left(C_1'C_1-C_2C_2'\right)\frac{(-eR)}{2} \quad (4\text{-}11)$$

and

$$\left\langle \chi_{px}(1)\middle|\hat{M}_z(1)\middle|\chi_{py}(1)\right\rangle=\frac{\gamma h}{2\pi i}\left\langle \chi_{px}(1)\middle|x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\middle|\chi_{py}(1)\right\rangle=\frac{\gamma h}{2\pi i}=\left\langle \chi_{px}(2)\middle|\hat{M}_z(1)\middle|\chi_{py}(2)\right\rangle \quad (4\text{-}12)$$

It follows that

$$\left\langle \varphi_e^0\middle|\hat{M}_z\middle|\varphi_{e'}^0\right\rangle=\left(C_1''^2+C_2'^2\right)\left(\frac{\gamma h}{2\pi i}\right)=\frac{\gamma h}{2\pi i} \quad (4\text{-}13)$$

and that

$$R_{eg}^{(3)}=\sum_{e'\in A_1}\sum_{e''\in B_2}\mathrm{Im}\left[\alpha_{e'g}\alpha_{e''e'}\left(\frac{\gamma h}{2\pi i}\right)\left(C_1C_1'-C_2C_2'\right)\left(-\frac{eR}{\sqrt{2}}\right)\right] \quad (4\text{-}14)$$

Finally we consider $R_{eg}^{(6)}$

$$R_{eg}^{(6)}=\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}\alpha_{e''g}^*\left\langle \varphi_e^0\middle|\hat{M}_z\middle|\varphi_{e'}^0\right\rangle\left\langle \varphi_{e'}^0\middle|\hat{\mu}_z\middle|\varphi_e^0\right\rangle\right] \quad (4\text{-}15)$$

where $\varphi_{e'''}^0$ denotes the $\sigma\rightarrow\pi_x^{**}$

$$\pi_x^{**}=C_1'''\chi_{px}(1)+C_2'''\chi_{px}(2) \quad (4\text{-}16)$$

$$\left\langle \varphi_{e'}^0\middle|\hat{\mu}_z\middle|\varphi_e^0\right\rangle=\left\langle \pi_x^{**}\middle|\hat{\mu}_z(1)\middle|\pi_x^*\right\rangle=C_1''C_1''\left\langle \chi_{px}(1)\middle|\hat{\mu}_z(1)\middle|\chi_{px}(1)\right\rangle+C_2''C_2''\left\langle \chi_{px}(2)\middle|\hat{\mu}_z(1)\middle|\chi_{px}(2)\right\rangle=\left(C_1''C_1''-C_2''C_2''\right)\left(-\frac{eR}{2}\right) \quad (4\text{-}17)$$

and

$$\left\langle \varphi_e^0\middle|\hat{M}_z\middle|\varphi_{e'}^0\right\rangle=\left\langle \pi_x^*\middle|\hat{M}_z(1)\middle|\pi_y^*\right\rangle=C_1''^2\left\langle \chi_{px}(1)\middle|\hat{M}_z(1)\middle|\chi_{py}(1)\right\rangle+C_2'^2\left\langle \chi_{px}(2)\middle|\hat{M}_z(1)\middle|\chi_{px}(2)\right\rangle=\frac{\gamma h}{2\pi i} \quad (4\text{-}18)$$

It follows that

$$R_{eg}^{(6)}=\sum_{e'\in B_2}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}\alpha_{e''g}^*\left(\frac{\gamma h}{2\pi i}\right)\left(C_1''C_1''-C_2'C_2'\right)\left(-\frac{eR}{2}\right)\right] \quad (4\text{-}19)$$

(B) $A_1\rightarrow B_2$

Notice that

$$R_{eg}^{(1)}=\sum_{e'\in A_1}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}^*\alpha_{e''e}\left\langle \varphi_e^0\middle|\hat{M}_x\middle|\varphi_g^0\right\rangle\left\langle \varphi_{e'}^0\middle|\hat{\mu}_x\middle|\varphi_{e'}^0\right\rangle\right] \quad (4\text{-}20)$$

where

$$\left\langle \varphi_{e'}^0\middle|\hat{\mu}_x\middle|\varphi_{e'}^0\right\rangle=\left\langle \pi_x^*\middle|\hat{\mu}_x(1)\middle|\sigma^*\right\rangle=C_1'C_1'\left\langle \chi_{px}(1)\middle|\hat{\mu}_x(1)\middle|\chi_s(1)\right\rangle+C_2'C_2''\left\langle \chi_{px}(2)\middle|\hat{\mu}_x(1)\middle|\chi_s(2)\right\rangle=\left(C_1'C_1''+C_2'C_2''\right)\frac{5e}{2\sqrt{3}\alpha} \quad (4\text{-}21)$$

and

$$\left\langle \varphi_e^0\middle|\hat{M}_x\middle|\varphi_g^0\right\rangle=\sqrt{2}\left\langle \pi_y^*\middle|\hat{M}_x(1)\middle|\sigma\right\rangle=\sqrt{2}\left(C_1C_1''\left\langle \chi_{py}(1)\middle|\hat{M}_x(1)\middle|\chi_s(1)\right\rangle+C_2C_2''\left\langle \chi_{py}(2)\middle|\hat{M}_x(1)\middle|\chi_s(2)\right\rangle\right)=\left(C_1C_1'-C_2C_2''\right)\left(-\frac{\gamma h}{2\pi i}\right)\frac{\alpha R}{2\sqrt{6}} \quad (4\text{-}22)$$

It follows that

$$R_{eg}^{(1)}=\sum_{e'\in A_1}\sum_{e''\in B_1}\mathrm{Im}\left[\alpha_{e'g}^*\alpha_{e''e}\left(C_1'C_1''+C_2'C_2'\right)\left(C_1C_1'-C_2C_2'\right)\times\left(-\frac{\gamma h}{2\pi i}\right)\frac{5eR}{12\sqrt{2}}\right] \quad (4\text{-}23)$$

Similarly we find

$$R_{eg}^{(2)}=0,\ R_{eg}^{(4)}=0,\ R_{eg}^{(5)}=0 \quad (4\text{-}24)$$

and

$$R_{eg}^{(3)} = \sum_{e' \in A_1} \sum_{e'' \in B_1} \mathrm{Im}\left[\alpha_{e'g}\alpha_{e''e}\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_{e'}^0 \right\rangle \left\langle \varphi_g^0 \middle| \hat{\mu}_z \middle| \varphi_{e''}^0 \right\rangle\right] \quad (4\text{-}25)$$

where

$$\left\langle \varphi_g^0 \middle| \hat{\mu}_z \middle| \varphi_{e''}^0 \right\rangle = \sqrt{2}\left\langle \chi_\sigma \middle| \hat{\mu}_z(1) \middle| \chi_{\sigma^*} \right\rangle = \sqrt{2}\left(C_1C_1' - C_2C_2'\right)\left(-\frac{eR}{2}\right) \quad (4\text{-}26)$$

and

$$\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_{e'}^0 \right\rangle = \left\langle \pi_y^* \middle| \hat{M}_z(1) \middle| \pi_x^* \right\rangle = -\frac{\gamma h}{2\pi i} \quad (4\text{-}27)$$

It follows that

$$R_{eg}^{(3)} = \sum_{e' \in A_1} \sum_{e'' \in B_1} \mathrm{Im}\left[\alpha_{e'g}\alpha_{e''e}\left(-\frac{\gamma h}{2\pi i}\right)\sqrt{2}\left(C_1C_1' - C_2C_2'\right)\left(-\frac{eR}{2}\right)\right] \quad (4\text{-}28)$$

Finally we consider

$$R_{eg}^{(6)} = \sum_{e' \in B_1} \sum_{e'' \in B_2} \mathrm{Im}\left[\alpha_{e'g}\alpha_{e''g}^*\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_{e'}^0 \right\rangle \left\langle \varphi_{e''}^0 \middle| \hat{\mu}_z \middle| \varphi_e^0 \right\rangle\right] \quad (4\text{-}29)$$

where

$$\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_{e'}^0 \right\rangle = \left\langle \pi_y^* \middle| \hat{M}_z(1) \middle| \pi_x^* \right\rangle = \left(-\frac{\gamma h}{2\pi i}\right) \quad (4\text{-}30)$$

and

$$\left\langle \varphi_{e''}^0 \middle| \hat{\mu}_z \middle| \varphi_e^0 \right\rangle = \left\langle \pi_y^{**} \middle| \hat{\mu}_z(1) \middle| \pi_y^* \right\rangle = \left(C_1'C_1'' - C_2'C_2''\right)\left(-\frac{eR}{2}\right) \quad (4\text{-}31)$$

It follows that

$$R_{eg}^{(6)} = \sum_{e' \in B_1} \sum_{e'' \in B_2} \mathrm{Im}\left[\alpha_{e'g}\alpha_{e''g}^*\left(-\frac{\gamma h}{2\pi i}\right)\left(C_1'C_1'' - C_2'C_2''\right)\left(-\frac{eR}{2}\right)\right] \quad (4\text{-}32)$$

As we can see from the above calculations, indeed the optical rotational strengths of $A_1 \rightarrow B_1$ and $A_1 \rightarrow B_2$ have opposite signs.

Next we shall apply our theory to explain the octant rule. For this purpose, we consider the case of $A_1 \rightarrow A_2$. In this case, we can easily show that

$$R_{eg}^{(1)} = 0; \; R_{eg}^{(4)} = 0 \quad (4\text{-}33)$$

Notice that

$$R_{eg}^{(2)} = \sum_{e' \in B_1} \sum_{e'' \in B_1} \mathrm{Im}\left[\alpha_{e'g}^*\alpha_{e''e}\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_g^0 \right\rangle \left\langle \varphi_{e'}^0 \middle| \hat{\mu}_z \middle| \varphi_{e''}^0 \right\rangle\right] +$$

$$\sum_{e' \in B_2} \sum_{e'' \in B_2} \mathrm{Im}\left[\alpha_{e'g}^*\alpha_{e''e}\left\langle \varphi_e^0 \middle| \hat{M}_z \middle| \varphi_g^0 \right\rangle \left\langle \varphi_{e'}^0 \middle| \hat{\mu}_z \middle| \varphi_{e''}^0 \right\rangle\right] \quad (4\text{-}34)$$

and that in $\alpha_{e''_{B_1} g_{A_1}}$ $\alpha_{e''_{B_1} e_{A_2}}$ we find that $\vec{\mu}_{e''_{B_1} g_{A_1}}$ is in the x-direction and that $\vec{\mu}_{e''_{B_1} e_{A_2}}$ is in the y-direction. In this case, for example for the camphor molecule the position change of the CH_3 group will bring in the change x $\rightarrow$ -x and thus we will have the change of $\alpha_{e''g}\alpha_{e'e}$ to $-\alpha_{e''g}\alpha_{e'e}$. In other words, we obtain the octant rule.

Quantitatively we have

$$\alpha_{e''g} = \frac{\left\langle e''G \middle| V_d \middle| gG \right\rangle}{E_g^0 - E_{e''}^0} \quad (4\text{-}35)$$

where G denotes the electronic state of the medium. Notice that

$$\left\langle e''G \middle| V_d \middle| gG \right\rangle = \frac{1}{\varepsilon R^3}\left[\left(\vec{\mu}_{e''g} \cdot \vec{\mu}_G\right) - \frac{3\left(\vec{\mu}_{e''g} \cdot \vec{R}\right)\left(\vec{\mu}_G \cdot \vec{R}\right)}{R^2}\right] \quad (4\text{-}36)$$

where $\vec{R}$ denotes the location of the CH_3 group from the chromophore group (in this case, the C=O group). Here $\vec{\mu}_g$ denotes the dipole moment of CH_3 group. We can easily show that the same rule applies to $R_{eg}^{(3)}$ and $R_{eg}^{(5)}$.

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Key Words

Thionine; Circular dichroism; Induced optical activity.

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