

Vibrational Circular Dichroism Spectroscopy

—The origin of VCD activity—

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振動円偏光二色性分光法

—VCD活性の起源—

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Abstract

The prediction of vibrational circular dichroism (VCD) spectra had been one of the most important and difficult problems in investigating the optical activity of chiral molecules. The theoretical explanation of the optical activity was successfully achieved by taking the vibrational state belonging to the electronic excited state into consideration. This implies that the phenomenon of VCD originates from the mixture of electronic states caused by the nuclear vibrational motions.

In the last part of this review, we report our results of experiments and theoretical calculations about (S)-(+)-2-butanol. The predicted spectra corresponding to OH bending mode of every conformer of this molecule can be classified into three types according to the relative conformation of OH group. The semi-empirical model based on the classical concept was developed and applied to analyze the relation between the VCD spectrum and molecular structure. As a result, the model was found to be effective to explain the feature of VCD spectrum of OH bending mode of this molecule.

要 旨

キラル分子の光学活性を考察する場合、振動円偏光二色性スペクトルを予測することは、最も重要で、かつ難しい問題の一つであった。この光学活性の理論的説明は、分子の電子励起状態にある振動状態を考慮に入れることで解決された。このことは、振動円偏光二色性という現象が、核の振動による電子状態の混合に由来することを示唆している。

本稿の最後では、(S)-(+)-2-butanolについて行った実験と理論計算の結果を報告

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した。この分子の各異性体の、OH変角振動に対応する計算スペクトルは、OH基の相対的な構造によって3つのタイプに分けられる。著者らは古典的概念に基づく半経験的モデルを作り、振動円偏光二色性スペクトルと分子の構造との間の関係についての解析を行った。その結果、本モデルがこの分子のOH変角振動の振動円偏光二色性スペクトルの特徴をよく説明することがわかった。

1. Introduction

The importance of chiral molecules has been well recognized, and much attention has been paid in the last few decades, particularly in biological aspects. The optical activity plays an important role in life. To investigate this property, various methods are being used. One of them is circular dichroism (CD) spectroscopy, which measures the difference of absorbance of left and right circularly polarized lights. The CD spectroscopy in the ultraviolet or visible region, i.e. electronic circular dichroism (ECD) spectroscopy, is widely used in order to deduce the absolute configuration, enantiomeric excess and so on, of the chiral molecules. But the ECD spectra are so simple that they do not give us much information about the molecular structure. There is also a restriction for the ECD spectroscopy, such that the sample molecule must have chromophore, so the method cannot be applied to the general chemicals which have no chromophore.

On the other hand, VCD spectroscopy which measures the circular dichroism in the infrared region give us a little complicated spectrum compared to the ECD spectroscopy. And the assignment of many bands of VCD spectrum is difficult, but the information about molecular properties obtained from the spectrum is very rich. Theoretically, every vibrational mode of chiral molecule has an optical activity. However, the signals of VCD spectrum are normally so weak, about four or five orders of magnitude less than those of vibrational absorption (IR) spectra. Therefore, the observation of the VCD spectrum has been rather difficult. In addition, a theory to explain the VCD phenomenon has not been matured, and a practical algorithm to predict the VCD spectrum has not fully developed until recently. Because of these reasons, there have not been enough experiences and reports in this field, especially about the relation between the spectra and molecular structures.

Very recently, however, the easy-to-handle apparatus of Fourier transform spectrometer has been developed, and is available commercially. Also the a priori theory of VCD has been established¹⁾, and made it possible to predict the spectra. The VCD spectroscopy is now the most attractive field that we can expect the great progress. In this review, we summarize some of the heuristic theories of VCD, and report our model applied to the OH bending mode of (S)-(+)-2-butanol. The semi-empirical model derived from the dynamic polarization model²⁾ could fairly well explain the characteristic features of VCD spectra of (S)-(+)-2-butanol. At the same

time, this model was found to possess some limits, and not necessarily be almighty. Although the model cannot be applied to every molecule and requires some more improvement, it might give us some hints to understand the origin of vibrational circular dichroism.

2. Vibrational Circular Dichroism

Under the Born-Oppenheimer (B-O) approximation, the wavefunction of the system can be written as

$$\Psi_{sN}(r, R) = \Psi_s(r; R) \Psi_N(R), \quad (2-1)$$

where r and R denote the coordinates of electrons and nuclei, respectively. The electronic wavefunction includes the nuclear coordinates as parameters. Let us assume that the nuclear wavefunction can be separated into the parts of vibrational motion and other nuclear motions. Then the nuclear wavefunction can be rewritten as

$$\Psi_N(R) = \Psi_v(R) \Psi_M(R). \quad (2-2)$$

We are now considering only the vibrational motion, and ignore the interaction with other nuclear motions. Then the wavefunction of the system under consideration can be rewritten as

$$\Psi_{sv}(r, R) = \Psi_s(r; R) \Psi_v(R). \quad (2-3)$$

In Eq. (2-3), the vibrational wavefunction $\Psi_v(R)$ belongs to the electronic state s . For the sake of simplicity, we will omit the variables r and R , hereafter.

In the previous study³⁾, we showed that the chiral molecules have non-zero value of the inner product of electric dipole and magnetic dipole transition moments, which causes the different absorption of left and right circularly polarized light. The factors which determine the intensity, including its sign, of circular dichroism (CD) spectrum are dipole strength and rotational strength. They are expressed as

$$D_{k',k} = \langle \Psi_{k'} | \boldsymbol{\mu} | \Psi_k \rangle^2, \quad (2-4)$$

and

$$R_{k',k} = \text{Im} \langle \Psi_k | \boldsymbol{\mu} | \Psi_{k'} \rangle \langle \Psi_{k'} | \boldsymbol{m} | \Psi_k \rangle, \quad (2-5)$$

respectively.

Now let us assume that the vibrational states included in Eqs. (2-4) and (2-5) belong to the same electronic state. Then the electric and magnetic dipole transition moments for the transition from vibrational state v to v' can be written as

$$\boldsymbol{\mu}_{v',v} = \langle \Psi_{v'} | \boldsymbol{\mu} | \Psi_v \rangle \quad (2-6)$$

and

$$\boldsymbol{m}_{v',v} = \langle \Psi_{v'} | \boldsymbol{m} | \Psi_v \rangle. \quad (2-7)$$

First, we will consider the electric dipole moment, which can be expanded as

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 Q + \frac{1}{2!} \left(\frac{\partial^2 \boldsymbol{\mu}}{\partial Q^2} \right)_0 Q^2 + \frac{1}{3!} \left(\frac{\partial^3 \boldsymbol{\mu}}{\partial Q^3} \right)_0 Q^3 + \dots \quad (2-8)$$

The subscript 0 denotes the equilibrium geometry, and Q refers to the normal coordinates. In the case of harmonic approximation, the second or higher orders in Eq. (2-8) can be neglected, therefore

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 Q. \quad (2-9)$$

Substituting Eq. (2-9) into Eq. (2-6), we can obtain

$$\begin{aligned} \boldsymbol{\mu}_{v,v} &= \langle \Psi_v | \boldsymbol{\mu}_0 + \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 Q | \Psi_v \rangle \\ &= \boldsymbol{\mu}_0 \langle \Psi_v | \Psi_v \rangle + \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 \langle \Psi_v | Q | \Psi_v \rangle. \end{aligned} \quad (2-10)$$

The second term of the right hand side of Eq. (2-10) has non-zero values only for the transitions of $v \rightarrow v \pm 1$, under the approximation of harmonic wavefunctions and harmonic electric dipole moment operator. In the case of $0 \rightarrow 1$ transition,

$$\boldsymbol{\mu}_{1,0} = \langle \Psi_1 | \boldsymbol{\mu} | \Psi_0 \rangle = \left(\frac{1}{2\alpha} \right)^{\frac{1}{2}} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0, \quad (2-11)$$

where $\alpha = \frac{2\pi\nu}{\hbar}$. (2-12)

Next, we will consider the magnetic dipole moment of the system consisted of point charges, which can be expressed as

$$\boldsymbol{m} = \frac{1}{2c} \sum_A eq_A (\boldsymbol{X}_A \times \dot{\boldsymbol{X}}_A), \quad (2-13)$$

where eq_A is the charge of the particle A (e being the unit charge), and \boldsymbol{X}_A is the positional vector of that particle. Eq. (2-13) is rewritten as

$$m_\alpha = \frac{1}{2c} \sum_A eq_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \dot{X}_{A\gamma}, \quad (2-14)$$

where α, β, γ denote x or y or z , and $\epsilon_{\alpha\beta\gamma}$ is the alternating tensor.

Magnetic dipole moment has one important property, that is the origin dependency. If we move the origin of the system along the vector $\boldsymbol{Y}^{(4)}$ whose components are all constants, the new magnetic dipole moment is expressed by

$$\begin{aligned}
\mathbf{m}' &= \frac{1}{2c} \sum_A eq_A \left((\mathbf{X}_A - \mathbf{Y}) \times \frac{\partial}{\partial t} (\mathbf{X}_A - \mathbf{Y}) \right) \\
&= \frac{1}{2c} \sum_A eq_A \left((\mathbf{X}_A \times \dot{\mathbf{X}}_A) - (\mathbf{Y} \times \dot{\mathbf{X}}_A) \right) \\
&= \mathbf{m} - \frac{1}{2c} \sum_A eq_A (\mathbf{Y} \times \dot{\mathbf{X}}_A) \\
&= \mathbf{m} - \frac{1}{2c} \sum_A \left(\mathbf{Y} \times \frac{\partial}{\partial t} (eq_A \mathbf{X}_A) \right) \\
&= \mathbf{m} - \frac{1}{2c} \left(\mathbf{Y} \times \frac{\partial}{\partial t} \left(\sum_A eq_A \mathbf{X}_A \right) \right) \\
&= \mathbf{m} - \frac{1}{2c} \left(\mathbf{Y} \times \frac{\partial \boldsymbol{\mu}}{\partial t} \right). \tag{2-15}
\end{aligned}$$

Then, each component of \mathbf{m}' can be expressed as

$$m'_\alpha = m_\alpha - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \left(\frac{\partial \mu_\gamma}{\partial t} \right). \tag{2-16}$$

The time derivative of the electric dipole moment, $\left(\frac{\partial \mu_\gamma}{\partial t} \right)$, can be written as

$$\frac{\partial \mu_\gamma}{\partial t} = \sum_A \sum_\delta \left(\frac{\partial \mu_\gamma}{\partial X_{A\delta}} \right) \left(\frac{\partial X_{A\delta}}{\partial t} \right) = \sum_A \sum_\delta \left(\frac{\partial \mu_\gamma}{\partial X_{A\delta}} \right) \dot{X}_{A\delta}. \tag{2-17}$$

By substituting Eqs. (2-14) and (2-17) into Eq. (2-16), we can get

$$\begin{aligned}
m'_\alpha &= \frac{1}{2c} \sum_A eq_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \dot{X}_{A\gamma} - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \left(\sum_A \sum_\delta \left(\frac{\partial \mu_\gamma}{\partial X_{A\delta}} \right) \dot{X}_{A\delta} \right) \\
&= \frac{1}{2c} \epsilon_{\alpha\beta\gamma} \left(\sum_A eq_A X_{A\beta} \dot{X}_{A\gamma} - Y_\beta \left(\sum_A \sum_\delta \left(\frac{\partial \mu_\gamma}{\partial X_{A\delta}} \right) \dot{X}_{A\delta} \right) \right). \tag{2-18}
\end{aligned}$$

Eq. (2-18) means that the magnetic dipole moment is a function of both positions and velocities of the particles. It also means that the magnetic dipole moment is generated by the variation of charge distribution, which accompanies the relative movement of the particles in a molecule, that is the vibrational motion.

The magnetic dipole moment is a function of positions and velocities, therefore it can be expanded by the normal coordinate Q and its conjugate momentum P . Both magnetic dipole moment and momentum change their signs by the time reversal operation, therefore the expansion of the magnetic dipole moment contains only the odd terms of derivatives with respect to P . On the other hand, the magnetic dipole moment at $\dot{\mathbf{X}} = 0$ is zero for a molecule in non-degenerate electronic states. Thus, the expansion of \mathbf{m} in Q and P can be written as

$$\begin{aligned} \mathbf{m} &= \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0 P + \frac{1}{2} \left(\frac{\partial^2 \mathbf{m}}{\partial P \partial Q} \right)_0 (PQ + QP) \\ &\quad + \frac{1}{2} \cdot \frac{1}{2!} \left(\frac{\partial^3 \mathbf{m}}{\partial P \partial Q^2} \right)_0 (PQ^2 + Q^2P) + \frac{1}{3!} \left(\frac{\partial^3 \mathbf{m}}{\partial P^3} \right)_0 P^3 + \dots \end{aligned} \quad (2-19)$$

Under the harmonic approximation, the magnetic dipole moment is simply expressed as

$$\mathbf{m} = \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0 P. \quad (2-20)$$

As well as the case of electric dipole moment, the magnetic dipole transition moment for the vibrational transition of 0→1 can be written as

$$\begin{aligned} m_{1,0} &= \langle \Psi_1 | \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0 P | \Psi_0 \rangle = \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0 \langle \Psi_1 | P | \Psi_0 \rangle \\ &= i\hbar \left(\frac{\alpha}{2} \right)^{\frac{1}{2}} \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0. \end{aligned} \quad (2-21)$$

where α is defined as that of Eq. (2-12).

Combining the results of Eqs. (2-11) and (2-21), we can calculate the vibrational dipole and rotational strengths as

$$D_{1,0} = \langle \Psi_1 | \boldsymbol{\mu} | \Psi_0 \rangle^2 = \frac{1}{2\alpha} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0^2 = \frac{\hbar}{4\pi\nu} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0^2, \quad (2-22)$$

$$\begin{aligned} R_{1,0} &= \text{Im} \langle \Psi_0 | \boldsymbol{\mu} | \Psi_1 \rangle \langle \Psi_1 | \mathbf{m} | \Psi_0 \rangle \\ &= \text{Im} \left(\left(\frac{1}{2\alpha} \right)^{\frac{1}{2}} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 \cdot i\hbar \left(\frac{\alpha}{2} \right)^{\frac{1}{2}} \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0 \right) \\ &= \frac{\hbar}{2} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q} \right)_0 \cdot \left(\frac{\partial \mathbf{m}}{\partial P} \right)_0. \end{aligned} \quad (2-23)$$

The hermiticity of $\boldsymbol{\mu}$ was used to derive Eq. (2-23).

In the practical calculation, we first evaluate $\frac{\partial \boldsymbol{\mu}}{\partial X}$ and $\frac{\partial \mathbf{m}}{\partial X}$ in the cartesian coordinates, then transform them into those in the normal coordinates. The transformation is accomplished as

$$\frac{\partial \boldsymbol{\mu}}{\partial Q} = \frac{\partial \boldsymbol{\mu}}{\partial X} \cdot \mathbf{L}_x, \quad (2-24)$$

$$\frac{\partial \mathbf{m}}{\partial P} = \frac{\partial \mathbf{m}}{\partial X} \cdot \mathbf{L}_x, \quad (2-25)$$

where \mathbf{L}_x is a transformation matrix satisfying the relation of $X = \mathbf{L}_x Q$. The tensors $\frac{\partial \boldsymbol{\mu}}{\partial X}$ and $\frac{\partial \mathbf{m}}{\partial X}$ are called atomic polar tensor (APT) and atomic axial tensor (AAT), respectively.

Many different approaches are introduced to evaluate APT and AAT. In most of

these approaches, the electric and magnetic dipole moments are separated into nuclear and electronic contributions, such as

$$\boldsymbol{\mu} = \boldsymbol{\mu}^N + \boldsymbol{\mu}^{\text{el}} = \sum_A eZ_A \mathbf{X}_A - e \sum_a \mathbf{X}_a, \quad (2-26)$$

$$\mathbf{m} = \mathbf{m}^N + \mathbf{m}^{\text{el}} = \frac{1}{2c} \sum_A eZ_A (\mathbf{X}_A \times \dot{\mathbf{X}}_A) - \frac{1}{2c} \sum_a e (\mathbf{X}_a \times \dot{\mathbf{X}}_a), \quad (2-27)$$

where eZ_A is the charge of the A th nucleus. The derivatives of nuclear parts can be evaluated in a straightforward way, like

$$\frac{\partial \mu_\alpha^N}{\partial X_{Ax}} = eZ_A \delta_{\alpha x}, \quad (2-28)$$

$$\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}} = \frac{1}{2c} eZ_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \delta_{\gamma x}. \quad (2-29)$$

As for electronic parts, a careful consideration must be paid, particularly in the case of AAT. Since the wavefunction of the molecule can be written as Eq. (2-3) under the B-O approximation, the electronic part of magnetic dipole transition moment for the vibrational transition from v to v' in the electronic state s can be written as

$$\mathbf{m}_{v',v}^{\text{el}} = \langle \Psi_s^0 \Psi_{v'}^0 | \mathbf{m}^{\text{el}} | \Psi_s^0 \Psi_v^0 \rangle = \langle \Psi_{v'}^0 | \langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_s^0 \rangle | \Psi_v^0 \rangle. \quad (2-30)$$

In a non-degenerate electronic state, the value of the matrix element $\langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_s^0 \rangle$ is zero. Therefore, the electronic contribution to the magnetic dipole transition moment becomes zero, which is obviously impossible to explain the actually observed optical activity of the molecule in a non-degenerate electronic state. That is, the B-O approximation breaks for the theory of VCD. Furthermore, the origin dependency of magnetic dipole moment makes another problem. Since the rotational strength is an observable intrinsic to the molecule under any physical condition independent of the choice of the coordinate. Therefore, it should have nothing to do with which origin we use to calculate the magnetic dipole moment derivatives.

To overcome these problems, many different approaches have been proposed. We would like to review some of them.

3. Coupled Oscillator Model

One of the simplest approaches avoiding the problems which arise from the B-O approximation is the coupled oscillator (CO) model. This model is a translation of the procedure developed previously for the electronic circular dichroism^{5), 6), 7)}, and was formulated by Holzwarth et al⁸⁾ to adapt to vibrational transitions.

This model is based on the hypothesis that the molecule in question is an optically active dimer composed of two identical diatomic molecules, A and B . These two diatomic molecules are considered to have a weak interaction. The total wavefunction of the monomer A in the vibrational state v are defined as Ψ_{Av} , and is supposed to be

in the electronic ground state. We assume that there is no structural overlap between the two monomeric parts, and therefore the wavefunctions of the two monomers are well separated from each other. Then the total wavefunction of the dimer in the vibrational ground state can be written as

$$\Phi_0 = \Psi_{A0} \Psi_{B0}. \quad (3-1)$$

The wavefunctions $\Psi_{A1} \Psi_{B0}$ and $\Psi_{A0} \Psi_{B1}$ of the vibrational excited state are degenerate. The group-theoretically independent wavefunctions can be generated by the symmetric and antisymmetric combination of the degenerate basis functions, $\Psi_{A1} \Psi_{B0}$ and $\Psi_{A0} \Psi_{B1}$. Therefore, the vibrational excited state wavefunctions Φ_1^\pm can be obtained as

$$\Phi_1^\pm = \frac{1}{\sqrt{2}} (\Psi_{A1} \Psi_{B0} \pm \Psi_{A0} \Psi_{B1}), \quad (3-2)$$

where + and - signs denote symmetric and antisymmetric, respectively.

Then the electric dipole transition moment for the transition of $0 \rightarrow 1$, $\mu_{1,0}^\pm$, is expressed as

$$\begin{aligned} \mu_{1,0}^\pm &= \langle \Phi_1^\pm | \mu_A + \mu_B | \Phi_0 \rangle \\ &= \frac{1}{\sqrt{2}} \langle (\Psi_{A1} \Psi_{B0} \pm \Psi_{A0} \Psi_{B1}) | \mu_A + \mu_B | \Psi_{A0} \Psi_{B0} \rangle, \end{aligned} \quad (3-3)$$

where μ_A and μ_B are the electric dipole moments of the monomer *A* and *B*.

Noting the relations

$$\mu_{A1,0} = \langle \Psi_{A1} | \mu_A | \Psi_{A0} \rangle \quad (3-4)$$

and

$$\mu_{B1,0} = \langle \Psi_{B1} | \mu_B | \Psi_{B0} \rangle, \quad (3-5)$$

Eq. (3-3) can be rewritten as

$$\mu_{1,0}^\pm = \frac{1}{\sqrt{2}} (\mu_{A1,0} \pm \mu_{B1,0}). \quad (3-6)$$

In the same way, the magnetic dipole transition moment for the transition of $0 \rightarrow 1$ is expressed as

$$\begin{aligned} m_{1,0}^\pm &= \langle \Phi_1^\pm | m_A + m_B | \Phi_0 \rangle \\ &= \frac{1}{\sqrt{2}} \langle \Phi_1^\pm | \sum_a \left(\frac{eq_a}{2M_a c} (X_a \times p_a) \right) + \sum_b \left(\frac{eq_b}{2M_b c} (X_b \times p_b) \right) | \Phi_0 \rangle. \end{aligned} \quad (3-7)$$

Notice that X_a , M_a , eq_a and p_a are the position, mass, charge and momentum of the *a*th particle of the monomer *A*, respectively, and X_b , M_b , eq_b and p_b are those of the *b*th particle of the monomer *B*. Those particles include both nuclei and electrons. Attention must be paid to the fact that the origins of magnetic dipole moments m_A and m_B , and positional vectors X_a and X_b are located at the center of mass (COM) of the dimer, or the molecule as a whole.

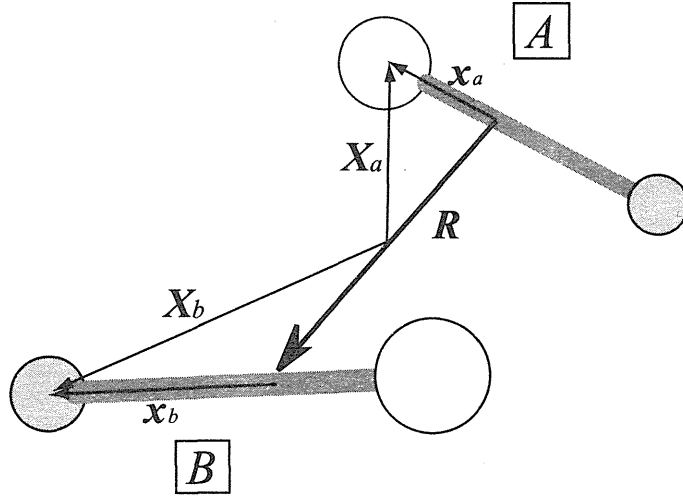


Fig.1 Hypothetical dimer composed of two identical diatomic molecules

Let us define the vector \mathbf{R} , which directs to the COM of the monomer B , originating from the COM of the monomer A . Also define the positional vector \mathbf{x}_a for the a th particle of the monomer A , whose origin is the COM of the monomer A , and the positional vector \mathbf{x}_b (see Fig.1). Then the equations relating the vectors, \mathbf{X} , \mathbf{x} and \mathbf{R} can be obtained as follows,

$$\mathbf{X}_a = \mathbf{x}_a - \frac{1}{2}\mathbf{R}, \quad (3-8)$$

$$\mathbf{X}_b = \mathbf{x}_b + \frac{1}{2}\mathbf{R}. \quad (3-9)$$

Assigning the above two relations into Eq. (3-3), we obtain the following equation,

$$\begin{aligned} \mathbf{m}_A + \mathbf{m}_B &= \sum_a \left\{ \frac{eq_a}{2M_a c} \left(\left(\mathbf{x}_a - \frac{1}{2}\mathbf{R} \right) \times \mathbf{p}_a \right) \right\} + \sum_b \left\{ \frac{eq_b}{2M_b c} \left(\left(\mathbf{x}_b + \frac{1}{2}\mathbf{R} \right) \times \mathbf{p}_b \right) \right\} \\ &= \sum_a \frac{eq_a}{2M_a c} (\mathbf{x}_a \times \mathbf{p}_a) - \frac{1}{4c} \sum_a \frac{eq_a}{M_a} (\mathbf{R} \times \mathbf{p}_a) \\ &\quad + \sum_b \frac{eq_b}{2M_b c} (\mathbf{x}_b \times \mathbf{p}_b) + \frac{1}{4c} \sum_b \frac{eq_b}{M_b} (\mathbf{R} \times \mathbf{p}_b) \\ &= \mathbf{m}_a + \mathbf{m}_b - \frac{1}{4c} \left(\sum_a \frac{eq_a}{M_a} (\mathbf{R} \times \mathbf{p}_a) - \sum_b \frac{eq_b}{M_b} (\mathbf{R} \times \mathbf{p}_b) \right), \end{aligned} \quad (3-10)$$

where \mathbf{m}_a and \mathbf{m}_b are the magnetic dipole moments of the monomer A and B , respectively, but the origins of them are now located to the COM of each monomer. The vectors \mathbf{x} and \mathbf{p} of each monomer are parallel since A and B are both diatomic molecules. Therefore, the outer product of \mathbf{x} and \mathbf{p} , that defines the \mathbf{m}_a or \mathbf{m}_b in Eq.

(3-10), becomes zero, that is

$$\mathbf{m}_a = \mathbf{m}_b = 0. \quad (3-11)$$

Substituting Eqs. (3-10) and (3-11) into Eq. (3-7), we can obtain

$$\begin{aligned} \mathbf{m}_{1,0}^\pm &= \frac{1}{\sqrt{2}} \langle \Phi_1^\pm | -\frac{1}{4c} \left(\sum_a \frac{eq_a}{M_a} (\mathbf{R} \times \mathbf{p}_a) - \sum_b \frac{eq_b}{M_b} (\mathbf{R} \times \mathbf{p}_b) \right) | \Phi_0 \rangle \\ &= -\frac{1}{4\sqrt{2}c} \langle \Phi_1^\pm | \left(\mathbf{R} \times \sum_a \frac{eq_a}{M_a} \mathbf{p}_a \right) - \left(\mathbf{R} \times \sum_b \frac{eq_b}{M_b} \mathbf{p}_b \right) | \Phi_0 \rangle \\ &= -\frac{1}{4\sqrt{2}c} \left(\mathbf{R} \times \langle \Phi_1^\pm | \sum_a \frac{eq_a}{M_a} \mathbf{p}_a - \sum_b \frac{eq_b}{M_b} \mathbf{p}_b | \Phi_0 \rangle \right). \end{aligned} \quad (3-12)$$

We write the frequency for the transition $0 \rightarrow 1$ as ν . Then, using the relation

$$\langle \Psi_1 | \mathbf{p} | \Psi_0 \rangle = -2\pi i M \nu \langle \Psi_1 | \mathbf{x} | \Psi_0 \rangle, \quad (3-13)$$

Eq. (3-12) can be written as

$$\begin{aligned} \mathbf{m}_{1,0}^\pm &= -\frac{1}{4\sqrt{2}c} \left(\mathbf{R} \times \langle \Phi_1^\pm | \sum_a \frac{eq_a}{M_a} (-2\pi i M_a \nu_a \mathbf{x}_a) - \sum_b \frac{eq_b}{M_b} (-2\pi i M_b \nu_b \mathbf{x}_b) | \Phi_0 \rangle \right) \\ &= \frac{\pi i}{2\sqrt{2}c} \left(\mathbf{R} \times \langle \Phi_1^\pm | \sum_a \nu_a (eq_a \mathbf{x}_a) - \sum_b \nu_b (eq_b \mathbf{x}_b) | \Phi_0 \rangle \right). \end{aligned} \quad (3-14)$$

The frequencies of the monomers, A and B , have the same value since the two monomeric parts are assumed to be identical. Therefore, Eq. (3-14) is rewritten as

$$\begin{aligned} \mathbf{m}_{1,0}^\pm &= \frac{\pi i \nu}{2\sqrt{2}c} \left(\mathbf{R} \times \langle \Phi_1^\pm | \sum_a eq_a \mathbf{x}_a - \sum_b eq_b \mathbf{x}_b | \Phi_0 \rangle \right) \\ &= \frac{\pi i \nu}{2\sqrt{2}c} \left(\mathbf{R} \times \langle \Phi_1^\pm | \boldsymbol{\mu}_a - \boldsymbol{\mu}_b | \Phi_0 \rangle \right) \\ &= \frac{\pi i \nu}{2\sqrt{2}c} \left(\mathbf{R} \times \langle (\Psi_{A1} \Psi_{B0} \pm \Psi_{A0} \Psi_{B1}) | \boldsymbol{\mu}_A - \boldsymbol{\mu}_B | \Psi_{A0} \Psi_{B0} \rangle \right). \end{aligned} \quad (3-15)$$

The origin-independency of electric dipole moment was used to derive the third row from the second in Eq. (3-15). By using Eqs. (3-4) and (3-5), which define the expectation value for the dipole moment operator, Eq. (3-15) can be simplified to

$$\mathbf{m}_{1,0}^\pm = \frac{\pi i \nu}{2\sqrt{2}c} \left(\mathbf{R} \times (\boldsymbol{\mu}_{A1,0} \mp \boldsymbol{\mu}_{B1,0}) \right). \quad (3-16)$$

By combining Eqs. (3-6) and (3-16), the rotational strength for the transition $0 \rightarrow 1$ is expressed as

$$\begin{aligned}
R_{1,0}^{\pm} &= \text{Im}(\boldsymbol{\mu}_{0,1}^{\pm} \cdot \mathbf{m}_{1,0}^{\pm}) \\
&= \text{Im} \left\{ \frac{1}{\sqrt{2}} (\boldsymbol{\mu}_{A0,1} \pm \boldsymbol{\mu}_{B0,1}) \cdot \frac{\pi i \nu}{2\sqrt{2}c} (\mathbf{R} \times (\boldsymbol{\mu}_{A1,0} \mp \boldsymbol{\mu}_{B1,0})) \right\} \\
&= \frac{\pi \nu}{4c} (\boldsymbol{\mu}_{A1,0} \pm \boldsymbol{\mu}_{B1,0}) \cdot (\mathbf{R} \times (\boldsymbol{\mu}_{A1,0} \mp \boldsymbol{\mu}_{B1,0})) \\
&= \frac{\pi \nu}{4c} \left\{ \begin{aligned} &\boldsymbol{\mu}_{A1,0} \cdot (\mathbf{R} \times \boldsymbol{\mu}_{A1,0}) \pm \boldsymbol{\mu}_{B1,0} \cdot (\mathbf{R} \times \boldsymbol{\mu}_{A1,0}) \\ &\mp \boldsymbol{\mu}_{A1,0} \cdot (\mathbf{R} \times \boldsymbol{\mu}_{B1,0}) - \boldsymbol{\mu}_{B1,0} \cdot (\mathbf{R} \times \boldsymbol{\mu}_{B1,0}) \end{aligned} \right\} \\
&= \pm \frac{\pi \nu}{2c} \mathbf{R} \cdot (\boldsymbol{\mu}_{A1,0} \times \boldsymbol{\mu}_{B1,0}). \tag{3-17}
\end{aligned}$$

The hermiticity $\boldsymbol{\mu}_{0,1} = \boldsymbol{\mu}_{1,0}$ was used to obtain the above equation.

From Eq. (3-17) we can expect to obtain the greater rotational strength when the angle made by two electric dipole moment vectors, $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$, becomes closer to 90 degrees, and get maximum value for perpendicular orientation. Eq. (3-17) also explains that the two VCD bands corresponding to $\Phi_0 \rightarrow \Phi_1^+$ and $\Phi_0 \rightarrow \Phi_1^-$ transitions have the equal intensities and opposite signs. The sign of the VCD band depends both on the symmetry of coupling and the relative geometry of two diatomic monomers.

The CO model is very simple and easy to understand. The derivation completely avoids the problems associated with the use of the B-O approximation and with the origin-dependency of magnetic dipole moment. However, it holds several fundamental difficulties⁹⁾. The CO model stands on an approximation of weak coupling between two parts in one molecule, and this is not obviously appropriate to treat normal vibrations of the molecule. Furthermore, we must divide a molecule into $3N-6$ parts to predict the rotational strengths for all vibrational transitions. At present, there are no tractable methods to treat this problem. Even if there were such a method, the exact vibrational-electronic states of all parts must be known. Moreover, the CO model treats only two parts out of $3N-6$ and ignores any interactions between the two parts in question and the rest parts of the molecule. Therefore, we need additional information, and then the simplicity of this model turns out to be lost.

However, for all these faults, the CO model expresses very clearly the physical aspects of VCD phenomenon. In this sense, it should be an attractive approach.

4. Analytical Method Using Perturbed Wavefunctions

The intermixture of the vibrational states belonging to the electronic excited states is needed to evaluate the electronic contribution to the magnetic dipole transition moment^{1), 4), 9)}. This is allowed through the breakdown of the B-O approximation. This implies that the modulation of the electron cloud caused by the nuclear vibrational motions stimulates the contribution of the electronic excited states to the ground state⁴⁾. This is now one of the most popular methods in calculation of the VCD properties¹⁰⁾. Furthermore, P. J. Stephens proposed a so-called distributed origin

gauge, and calculated the origin-independent rotational strength¹¹⁾.

As we mentioned earlier, the wavefunction of a molecule can be written as

$$\Psi_{sv}^0 = \Psi_s^0 \Psi_v^0. \quad (4-1)$$

Let us express H_0 as a part of the total Hamiltonian excluded a part of the nuclear kinetic energy. Then, the total Hamiltonian H can be expanded by k th normal coordinate Q_k as

$$\begin{aligned} H &= H_0 + \sum_k \left(\frac{\partial H}{\partial Q_k} \right)_0 Q_k + \dots \\ &= H_0 + H_1 + \dots \end{aligned} \quad (4-2)$$

Taking the first order term H_1 as a perturbation, the wavefunction given in Eq. (4-1) is corrected as

$$\Psi_{sv} = \Psi_s^0 \Psi_v^0 + \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \Psi_n^0 \Psi_{v'}^0}{(E_s^0 + E_v^0) - (E_n^0 + E_{v'}^0)}. \quad (4-3)$$

Here the vibrational wavefunctions Ψ_v^0 and $\Psi_{v'}^0$ belong to the electronic states s and n , respectively. The electronic part of the electric dipole transition moment for the transition from the state sv to sv' can be written, using the above-mentioned corrected wavefunction, as

$$\begin{aligned} \mu_{sv',v}^{\text{el}} &= \langle \Psi_{sv'} | \boldsymbol{\mu}^{\text{el}} | \Psi_{sv} \rangle \\ &= \langle \Psi_s^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \Psi_v^0 \rangle \\ &\quad + \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \Psi_{v'}^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_{v'}^0)} \\ &\quad + \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_n^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \Psi_v^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_{v'}^0)} \\ &\quad + \sum_{n \neq s} \sum_{m \neq s} \sum_{v''} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_m^0 \Psi_{v''}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_n^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_m^0 \Psi_{v''}^0 \rangle}{((E_s^0 + E_{v'}^0) - (E_n^0 + E_{v'}^0))((E_s^0 + E_{v'}^0) - (E_m^0 + E_{v''}^0))}. \end{aligned} \quad (4-4)$$

Let us assume that the vibrational wavefunctions are the same in both the ground and excited electronic states. The electronic and vibrational wavefunctions of the expectation value for the electric dipole moment can be separated under the B-O approximation. And, the first term of the right hand side of Eq. (4-4) turns out to be zero since we are thinking the vibrational transition, that is $v \neq v'$, therefore we obtain

$$\langle \Psi_s^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \Psi_v^0 \rangle = \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle \langle \Psi_{v'}^0 | \Psi_v^0 \rangle = 0. \quad (4-5)$$

The second term of Eq. (4-4) is also treated in the same way as above, and the terms which are left non-zero in the summation by the vibrational quantum number are those of $v'' = v'$. In the case of the third term, the non-zero terms are for $v'' = v$. As a result, the second and third terms of Eq. (4-4) can be rewritten as

$$\begin{aligned}
& \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \Psi_{v'}^0 \rangle}{(E_s^0 + E_v^0) - (E_n^0 + E_{v'}^0)} \\
&= \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \rangle \langle \Psi_{v'}^0 | \Psi_{v'}^0 \rangle}{(E_s^0 + E_v^0) - (E_n^0 + E_{v'}^0)} \\
&= \sum_{n \neq s} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \rangle}{(E_s^0 + E_v^0) - (E_n^0 + E_{v'}^0)}. \tag{4-6}
\end{aligned}$$

$$\begin{aligned}
& \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_n^0 \Psi_{v'}^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \Psi_v^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_v^0)} \\
&= \sum_{n \neq s} \sum_{v'} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_n^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle \langle \Psi_{v'}^0 | \Psi_v^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_v^0)} \\
&= \sum_{n \neq s} \frac{\langle \Psi_n^0 \Psi_v^0 | H_1 | \Psi_s^0 \Psi_{v'}^0 \rangle \langle \Psi_n^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_v^0)}. \tag{4-7}
\end{aligned}$$

The fourth term is much smaller than the second or third terms. This can be easily understood by noting that the fourth term is a product of matrix elements with perturbing Hamiltonian, H_1 , and also that the denominator of the fourth term is approximately square of those of the second and third terms. Therefore the fourth term can be ignored. Then Eq. (4-4) can be simplified to

$$\begin{aligned}
\boldsymbol{\mu}_{v',v}^{\text{el}} &= \sum_{n \neq s} \frac{\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \rangle}{(E_s^0 + E_v^0) - (E_n^0 + E_{v'}^0)} \\
&+ \sum_{n \neq s} \frac{\langle \Psi_n^0 \Psi_v^0 | H_1 | \Psi_s^0 \Psi_{v'}^0 \rangle \langle \Psi_n^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle}{(E_s^0 + E_{v'}^0) - (E_n^0 + E_v^0)}. \tag{4-8}
\end{aligned}$$

The denominator of Eq. (4-8) can be written as $(1 \pm x)(E_s^0 - E_n^0)$, where $x = \frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0}$. Since $x \ll 1$, the approximate expression of $(1 \pm x)^{-1} \approx 1 \mp x$ can be applied. Then, Eq. (4-8) can again be rewritten as follows.

$$\begin{aligned}
\boldsymbol{\mu}_{v',v}^{\text{el}} &= \sum_{n \neq s} \langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \rangle \left(1 - \frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0} \right) \frac{1}{E_s^0 - E_n^0} \\
&+ \sum_{n \neq s} \langle \Psi_n^0 \Psi_v^0 | H_1 | \Psi_s^0 \Psi_{v'}^0 \rangle \langle \Psi_n^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle \left(1 + \frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0} \right) \frac{1}{E_s^0 - E_n^0}. \tag{4-9}
\end{aligned}$$

When matrix elements are all real in Eq. (4-9), the relation of $\langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_n^0 \rangle = \langle \Psi_n^0 | \boldsymbol{\mu}^{\text{el}} | \Psi_s^0 \rangle$ holds, then the terms which contain $\frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0}$ vanish. Using the relation of Eq. (4-2), the matrix element $\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle$ can be written as

$$\begin{aligned}
\langle \Psi_n^0 \Psi_{v'}^0 | H_1 | \Psi_s^0 \Psi_{v'}^0 \rangle &= \langle \Psi_n^0 \Psi_{v'}^0 | \sum_k \left(\frac{\partial H}{\partial Q_k} \right) Q_k | \Psi_s^0 \Psi_{v'}^0 \rangle \\
&= \sum_k \langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_{v'}^0 | Q_k | \Psi_{v'}^0 \rangle.
\end{aligned} \tag{4-10}$$

Noting the relation $\langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle = \langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle$, the two parts of Eq. (4-9) can be combined to

$$\mu_{v_k, v_k}^{\text{el}} = 2 \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | \mu^{\text{el}} | \Psi_n^0 \rangle}{E_s^0 - E_n^0} \cdot \langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle. \tag{4-11}$$

Making use of the first order perturbation theory, the following relation is obtained,

$$\begin{aligned}
\Psi_s &= \Psi_s^0 + \sum_{n \neq s} \frac{\langle \Psi_n^0 | H_1 | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\
&= \Psi_s^0 + \sum_{n \neq s} \sum_k \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} Q_k | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\
&= \Psi_s^0 + \sum_{n \neq s} \sum_k Q_k \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0.
\end{aligned} \tag{4-12}$$

Differentiating Eq. (4-12) by Q_k , we can obtain

$$\frac{\partial \Psi_s}{\partial Q_k} = \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0. \tag{4-13}$$

Substituting this equation into Eq. (4-11), electronic part of the electric dipole transition moment can be written as

$$\mu_{v_k, v_k}^{\text{el}} = 2 \langle \Psi_s^0 | \mu^{\text{el}} | \frac{\partial \Psi_s}{\partial Q_k} \rangle \cdot \langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle. \tag{4-14}$$

In the harmonic case, $\mu_{v_k, v_k}^{\text{el}}$ can also be written as

$$\begin{aligned}
\mu_{v_k, v_k}^{\text{el}} &= \langle \Psi_{v_k}^0 | \mu_0^{\text{el}} + \left(\frac{\partial \mu^{\text{el}}}{\partial Q_k} \right) Q_k | \Psi_{v_k}^0 \rangle \\
&= \mu_0^{\text{el}} \langle \Psi_{v_k}^0 | \Psi_{v_k}^0 \rangle + \left(\frac{\partial \mu^{\text{el}}}{\partial Q_k} \right) \langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle \\
&= \left(\frac{\partial \mu^{\text{el}}}{\partial Q_k} \right) \langle \Psi_{v_k}^0 | Q_k | \Psi_{v_k}^0 \rangle.
\end{aligned} \tag{4-15}$$

Comparing Eqs. (4-14) and (4-15), the electronic part of the electric dipole moment derivative is given as

$$\frac{\partial \mu^{\text{el}}}{\partial Q_k} = 2 \langle \Psi_s^0 | \mu^{\text{el}} | \frac{\partial \Psi_s}{\partial Q_k} \rangle. \tag{4-16}$$

The above equation is expressed by cartesian coordinate as

$$\begin{aligned}
\frac{\partial \boldsymbol{\mu}^{\text{el}}}{\partial \mathbf{X}} &= \sum_k \frac{\partial \boldsymbol{\mu}^{\text{el}}}{\partial Q_k} \cdot \frac{\partial Q_k}{\partial \mathbf{X}} \\
&= 2 \sum_k \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \frac{\partial \Psi_s}{\partial Q_k} \rangle \cdot \frac{\partial Q_k}{\partial \mathbf{X}} \\
&= 2 \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \sum_k \frac{\partial \Psi_s}{\partial Q_k} \cdot \frac{\partial Q_k}{\partial \mathbf{X}} \rangle \\
&= 2 \langle \Psi_s^0 | \boldsymbol{\mu}^{\text{el}} | \frac{\partial \Psi_s}{\partial \mathbf{X}} \rangle.
\end{aligned} \tag{4-17}$$

Then, from Eqs. (2-28) and (4-17), we can obtain the elements of APT,

$$\begin{aligned}
\frac{\partial \mu_\alpha}{\partial X_{A\alpha}} &= \frac{\partial \mu_\alpha^{\text{N}}}{\partial X_{A\alpha}} + \frac{\partial \mu_\alpha^{\text{el}}}{\partial X_{A\alpha}} \\
&= eZ_{A\alpha} \delta_{\alpha\alpha} + 2 \text{Re} \langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \frac{\partial \Psi_s}{\partial X_{A\alpha}} \rangle.
\end{aligned} \tag{4-18}$$

The procedure for evaluating AAT fairly resembles the one for APT. Starting from the perturbed wavefunction given as Eq. (4-3), we can obtain the electronic part of magnetic dipole transition moment for the transition from the state sv to sv' as an analogue of Eq. (4-9),

$$\begin{aligned}
\mathbf{m}_{v',v}^{\text{el}} &= \sum_{n \neq s} \langle \Psi_n^0 \Psi_v^0 | H_1 | \Psi_s^0 \Psi_v^0 \rangle \langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_n^0 \rangle \left(1 - \frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0} \right) \frac{1}{E_s^0 - E_n^0} \\
&\quad + \sum_{n \neq s} \langle \Psi_n^0 \Psi_v^0 | H_1 | \Psi_s^0 \Psi_{v'}^0 \rangle \langle \Psi_n^0 | \mathbf{m}^{\text{el}} | \Psi_s^0 \rangle \left(1 + \frac{E_n^0 - E_{v'}^0}{E_s^0 - E_n^0} \right) \frac{1}{E_s^0 - E_n^0}.
\end{aligned} \tag{4-19}$$

Since \mathbf{m} is purely imaginary, the hermiticity of the operator requires the relation of

$$\langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_n^0 \rangle = - \langle \Psi_n^0 | \mathbf{m}^{\text{el}} | \Psi_s^0 \rangle. \tag{4-20}$$

Therefore, the terms in Eq. (4-19) which do not contain $\frac{E_v^0 - E_{v'}^0}{E_s^0 - E_n^0}$ vanish. Then we can obtain the relation analogous to Eq. (4-11) as follows,

$$\begin{aligned}
\mathbf{m}_{v'_k, v_k}^{\text{el}} &= \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2} (E_{v'_k}^0 - E_{v_k}^0) (\langle \Psi_{v'_k}^0 | Q_k | \Psi_{v_k}^0 \rangle + \langle \Psi_{v_k}^0 | Q_k | \Psi_{v'_k}^0 \rangle) \\
&= \sum_{n \neq s} \frac{2(E_{v'_k}^0 - E_{v_k}^0)}{(E_s^0 - E_n^0)^2} \langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_n^0 \rangle \langle \Psi_{v'_k}^0 | Q_k | \Psi_{v_k}^0 \rangle \\
&= \sum_{n \neq s} \frac{2i(E_{v'_k}^0 - E_{v_k}^0)}{(E_s^0 - E_n^0)^2} \langle \Psi_{v'_k}^0 | Q_k | \Psi_{v_k}^0 \rangle \text{Im} \langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | \mathbf{m}^{\text{el}} | \Psi_n^0 \rangle.
\end{aligned} \tag{4-21}$$

In the case of $v' = v + 1$, we obtain the energy difference as $E_{v'_k}^0 - E_{v_k}^0 = h\nu_k$. The matrix elements involving the operators Q and P satisfy the next relations,

$$\begin{aligned}\langle \Psi_{(v+1)_k}^0 | Q_k | \Psi_{v_k}^0 \rangle &= -\frac{i}{\alpha \hbar} \langle \Psi_{(v+1)_k}^0 | P_k | \Psi_{v_k}^0 \rangle \\ &= -\frac{i}{2\pi\nu_k} \langle \Psi_{(v+1)_k}^0 | P_k | \Psi_{v_k}^0 \rangle.\end{aligned}\quad (4-22)$$

Assigning this relation into Eq. (4-21), we obtain

$$\begin{aligned}m_{v'_k, v_k}^{\text{el}} &= \sum_{n \neq s} \frac{2i\hbar\nu_k}{(E_s^0 - E_n^0)^2} \left(-\frac{i}{2\pi\nu_k} \langle \Psi_{v'_k}^0 | P_k | \Psi_{v_k}^0 \rangle \right) \text{Im} \langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | m^{\text{el}} | \Psi_n^0 \rangle \\ &= \sum_{n \neq s} \frac{1}{(E_s^0 - E_n^0)^2} \cdot \frac{\hbar}{\pi} \langle \Psi_{v'_k}^0 | P_k | \Psi_{v_k}^0 \rangle \text{Im} \langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle \langle \Psi_s^0 | m^{\text{el}} | \Psi_n^0 \rangle.\end{aligned}\quad (4-23)$$

Let us take H_1 in the Eq. (4-12) as $-m_\alpha B_\alpha$, that is the perturbation by the external magnetic field. Notice that B_α denotes the component of magnetic field vector \mathbf{B} , and α refers to the cartesian coordinate, x or y or z . Then the derived expression for the perturbed wavefunction is

$$\begin{aligned}\Psi_s &= \Psi_s^0 + \sum_{n \neq s} \frac{\langle \Psi_n^0 | H_1 | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\ &= \Psi_s^0 - \sum_{n \neq s} \frac{\langle \Psi_n^0 | m_\alpha B_\alpha | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\ &= \Psi_s^0 - \sum_{n \neq s} \frac{\langle \Psi_n^0 | m_\alpha^N B_\alpha + m_\alpha^{\text{el}} B_\alpha | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\ &= \Psi_s^0 - \sum_{n \neq s} \frac{\langle \Psi_n^0 | m_\alpha^{\text{el}} B_\alpha | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 - m_\alpha^N B_\alpha \sum_{n \neq s} \frac{\langle \Psi_n^0 | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \\ &= \Psi_s^0 + B_\alpha \sum_{n \neq s} \frac{\langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_n^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0.\end{aligned}\quad (4-24)$$

Differentiation of this equation by B_α is given by

$$\frac{\partial \Psi_s}{\partial B_\alpha} = \sum_{n \neq s} \frac{\langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_n^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0.\quad (4-25)$$

From Eqs. (4-13), (4-23) and (4-25), the elements of electronic contributions to the magnetic dipole transition moment can be summarized as

$$\begin{aligned}m_{\alpha v'_k, v_k}^{\text{el}} &= \sum_{n \neq s} \frac{\hbar}{\pi} \langle \Psi_{v'_k}^0 | P_k | \Psi_{v_k}^0 \rangle \text{Im} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial Q_k} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \langle \Psi_n^0 | \Psi_s^0 \rangle \cdot \frac{\langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_n^0 \rangle}{E_s^0 - E_n^0} \\ &= \frac{\hbar}{\pi} \langle \Psi_{v'_k}^0 | P_k | \Psi_{v_k}^0 \rangle \text{Im} \left\langle \frac{\partial \Psi_s}{\partial Q_k} \middle| \frac{\partial \Psi_s}{\partial B_\alpha} \right\rangle.\end{aligned}\quad (4-26)$$

In the harmonic case, $m_{\alpha v'_k, v_k}^{\text{el}}$ can also be expressed as

$$m_{\alpha v'_k, v_k}^{\text{el}} = \langle \Psi_{v'_k}^0 | \left(\frac{\partial m_\alpha^{\text{el}}}{\partial P_k} \right) P_k | \Psi_{v_k}^0 \rangle = \left(\frac{\partial m_\alpha^{\text{el}}}{\partial P_k} \right) \langle \Psi_{v'_k}^0 | P_k | \Psi_{v_k}^0 \rangle.\quad (4-27)$$

By comparing Eqs. (4-26) and (4-27), we can get the electronic part of the magnetic dipole moment derivative as

$$\frac{\partial m_\alpha^{\text{el}}}{\partial P_k} = \frac{h}{\pi} \text{Im} \left\langle \frac{\partial \Psi_s}{\partial Q_k} \left| \frac{\partial \Psi_s}{\partial B_\alpha} \right. \right\rangle. \quad (4-28)$$

This formula is expressed in cartesian coordinate as

$$\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{Ax}} = \frac{h}{\pi} \text{Im} \left\langle \frac{\partial \Psi_s}{\partial X_{Ax}} \left| \frac{\partial \Psi_s}{\partial B_\alpha} \right. \right\rangle. \quad (4-29)$$

Then, from Eqs. (2-29) and (4-29), we can obtain the elements of AAT as

$$\begin{aligned} \frac{\partial m_\alpha}{\partial \dot{X}_{Ax}} &= \frac{\partial m_\alpha^{\text{N}}}{\partial \dot{X}_{Ax}} + \frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{Ax}} \\ &= \frac{1}{2c} e Z_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \delta_{\gamma\alpha} + \frac{h}{\pi} \text{Im} \left\langle \frac{\partial \Psi_s}{\partial X_{Ax}} \left| \frac{\partial \Psi_s}{\partial B_\alpha} \right. \right\rangle. \end{aligned} \quad (4-30)$$

The rotational strength for k th normal mode obtained from Eqs. (4-16) and (4-28) is depend on which origin we choose because of the origin dependency of \mathbf{B} . However, as we mentioned earlier, the rotational strength should be independent of the molecular origin since it is an observable independent of the position in space. One of the solutions is given by the concept of distributed origin gauge¹¹⁾.

Here we show again the same equation as Eq. (2-26), the nuclear and electronic contributions to the electric dipole moment,

$$\boldsymbol{\mu} = \boldsymbol{\mu}^{\text{N}} + \boldsymbol{\mu}^{\text{el}} = \sum_A e Z_A \mathbf{X}_A - e \sum_a \mathbf{X}_a. \quad (4-31)$$

Assume that we move the molecular origin from \mathbf{O} to \mathbf{Y} . Then the nuclear part of the new electric dipole moment is written as

$$\left(\boldsymbol{\mu}_a^{\text{N}} \right)^{\mathbf{Y}} = \sum_A e Z_A (\mathbf{X}_{Aa} - \mathbf{Y}_a) = \left(\boldsymbol{\mu}_a^{\text{N}} \right)^{\mathbf{O}} - \sum_A e Z_A \mathbf{Y}_a. \quad (4-32)$$

The superscript \mathbf{O} and \mathbf{Y} mean the molecular origins before and after the displacement. Then, the elements of the nuclear part of APT tensor after the displacement of the origin, that is the derivative of electric dipole moment by cartesian coordinate, are given by

$$\left(\frac{\partial \boldsymbol{\mu}_a^{\text{N}}}{\partial X_{Ax}} \right)^{\mathbf{Y}} = \left(\frac{\partial \boldsymbol{\mu}_a^{\text{N}}}{\partial X_{Ax}} \right)^{\mathbf{O}}, \quad (4-33)$$

which are apparently origin-independent.

As for the electronic part of the electric dipole moment, the expectation value in the electronic state s is expressed as

$$\langle \Psi_s | \boldsymbol{\mu}^{\text{el}} | \Psi_s \rangle. \quad (4-34)$$

The expansion of the Hamiltonian H by cartesian coordinate X_{Ax} is

$$\begin{aligned} H &= H_0 + \sum_{A,x} \left(\frac{\partial H}{\partial X_{Ax}} \right)_0 X_{Ax} + \cdots \\ &= H_0 + H_1 + \cdots, \end{aligned} \quad (4-35)$$

which is analogous to Eq. (4-2). The analogous expression to Eq. (4-13) is

$$\frac{\partial \Psi_s}{\partial X_{Ax}} = \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{Ax}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0. \quad (4-36)$$

Using this relation, the electronic wavefunction Ψ_s is expanded as

$$\begin{aligned} \Psi_s &= \Psi_s^0 + \sum_{A,X} \left(\frac{\partial \Psi_s}{\partial X_{Ax}} \right) X_{Ax} + \dots \\ &= \Psi_s^0 + \left(\sum_{A,X} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{Ax}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \right) X_{Ax} + \dots \end{aligned} \quad (4-37)$$

By ignoring the second or higher order terms of Eq. (4-37), the electronic part of the APT, which is the derivative of Eq. (4-34) by cartesian coordinate, is derived as follows,

$$\begin{aligned} \frac{\partial \mu_\alpha^{\text{el}}}{\partial X_{Ax}} &= \frac{\partial}{\partial X_{Ax}} \langle \Psi_s | \mu_\alpha^{\text{el}} | \Psi_s \rangle \\ &= \frac{\partial}{\partial X_{Ax}} \langle \Psi_s^0 + \left(\sum_{B,\gamma} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{B\gamma}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \right) X_{B\gamma} | \mu_\alpha^{\text{el}} | \Psi_s^0 + \left(\sum_{B,\gamma} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{B\gamma}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \right) X_{B\gamma} \rangle \\ &= \frac{\partial}{\partial X_{Ax}} \left\{ \langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \Psi_s^0 \rangle \right. \\ &\quad + \sum_{B,\gamma} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{B\gamma}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \left(\langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \Psi_n^0 \rangle + \langle \Psi_n^0 | \mu_\alpha^{\text{el}} | \Psi_s^0 \rangle \right) X_{B\gamma} \\ &\quad \left. + \sum_{B,\gamma} \sum_{C,\delta} \sum_{m \neq s} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{B\gamma}} | \Psi_s^0 \rangle \langle \Psi_m^0 | \frac{\partial H}{\partial X_{C\delta}} | \Psi_s^0 \rangle}{(E_s^0 - E_n^0)(E_s^0 - E_m^0)} \langle \Psi_n^0 | \mu_\alpha^{\text{el}} | \Psi_m^0 \rangle X_{B\gamma} X_{C\delta} \right\}. \end{aligned} \quad (4-38)$$

The value of the third term in Eq. (4-38) is much smaller than that of the second term, and the third term can be ignored. Noting the relation $\langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \Psi_n^0 \rangle = \langle \Psi_n^0 | \mu_\alpha^{\text{el}} | \Psi_s^0 \rangle$, the Eq. (4-38) is rewritten as

$$\frac{\partial \mu_\alpha^{\text{el}}}{\partial X_{Ax}} = 2 \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{Ax}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \Psi_n^0 \rangle. \quad (4-39)$$

Let us move the molecular origin from O to Y . Then, the electronic part of the new electric dipole moment in Eq. (4-31) is

$$(\mu_\alpha^{\text{el}})^Y = -e \sum_a (X_{a\alpha} - Y_\alpha) = (\mu_\alpha^{\text{el}})^O + \sum_a e Y_\alpha. \quad (4-40)$$

Then the matrix element $\langle \Psi_s^0 | \mu_\alpha^{\text{el}} | \Psi_n^0 \rangle$ for the new origin can be written as

$$\begin{aligned}
\langle \Psi_s^0 | (\mu_\alpha^{\text{el}})^y | \Psi_n^0 \rangle &= \langle \Psi_s^0 | (\mu_\alpha^{\text{el}})^o + \sum_\alpha eY_\alpha | \Psi_n^0 \rangle \\
&= \langle \Psi_s^0 | (\mu_\alpha^{\text{el}})^o | \Psi_n^0 \rangle + \sum_\alpha eY_\alpha \langle \Psi_s^0 | \Psi_n^0 \rangle \\
&= \langle \Psi_s^0 | (\mu_\alpha^{\text{el}})^o | \Psi_n^0 \rangle.
\end{aligned} \tag{4-41}$$

It is apparent that $\frac{\partial H}{\partial X_{A\alpha}}$ is origin-independent. Therefore, the next relation can be derived from Eqs. (4-39) and (4-41),

$$\left(\frac{\partial \mu_\alpha^{\text{el}}}{\partial X_{A\alpha}} \right)^y = \left(\frac{\partial \mu_\alpha^{\text{el}}}{\partial X_{A\alpha}} \right)^o. \tag{4-42}$$

Combining Eqs. (4-33) and (4-41), which expresses the origin independence of the nuclear part and the electronic part of APT, we obtain

$$\left(\frac{\partial \mu_\alpha}{\partial X_{A\alpha}} \right)^y = \left(\frac{\partial \mu_\alpha}{\partial X_{A\alpha}} \right)^o. \tag{4-43}$$

Thus, APT is origin-independent.

In normal coordinate, this can be written as

$$\left(\frac{\partial \mu_\alpha}{\partial Q_k} \right)^y = \left(\frac{\partial \mu_\alpha}{\partial Q_k} \right)^o. \tag{4-44}$$

Let us now discuss about the effects of the molecular origin on AAT, and then, on the rotational strength.

From Eqs. (2-29) and (4-29), the nuclear and electronic parts of AAT are written as

$$\frac{\partial m_\alpha^{\text{N}}}{\partial \dot{X}_{A\alpha}} = \frac{1}{2c} eZ_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \delta_{\gamma\alpha} \tag{4-45}$$

and

$$\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\alpha}} = -2i\hbar \left\langle \frac{\partial \Psi_s}{\partial X_{A\alpha}} \middle| \frac{\partial \Psi_s}{\partial B_\alpha} \right\rangle, \tag{4-46}$$

respectively. Substituting Eqs. (4-25) and (4-36) into Eq. (4-46), the electronic part of AAT can be obtained as

$$\begin{aligned}
\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\alpha}} &= -2i\hbar \left\langle \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\alpha}} | \Psi_s^0 \rangle}{E_s^0 - E_n^0} \Psi_n^0 \middle| \sum_{m \neq s} \frac{\langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_m^0 \rangle}{E_s^0 - E_m^0} \Psi_m^0 \right\rangle \\
&= -2i\hbar \sum_{n \neq s} \sum_{m \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\alpha}} | \Psi_s^0 \rangle \langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_m^0 \rangle}{(E_s^0 - E_n^0)(E_s^0 - E_m^0)} \langle \Psi_n^0 | \Psi_m^0 \rangle \\
&= -2i\hbar \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\alpha}} | \Psi_s^0 \rangle \langle \Psi_s^0 | m_\alpha^{\text{el}} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2}.
\end{aligned} \tag{4-47}$$

The orthonormality of Ψ_n^0 was used to derive the third term from the second term in Eq. (4-47).

Let us move the molecular origin from \mathbf{O} to \mathbf{Y} . Then, from Eqs. (2-28), (4-33), and (4-46), the nuclear contribution to AAT can be expressed as

$$\begin{aligned} \left(\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}} \right)^Y &= \frac{1}{2c} e Z_A \epsilon_{\alpha\beta\gamma} (X_{A\beta} - Y_\beta) \delta_{\gamma\alpha} \\ &= \frac{1}{2c} e Z_A \epsilon_{\alpha\beta\gamma} X_{A\beta} \delta_{\gamma\alpha} - \frac{1}{2c} e Z_A \epsilon_{\alpha\beta\gamma} Y_\beta \delta_{\gamma\alpha} \\ &= \left(\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}} \right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma^N}{\partial X_{Ax}}, \end{aligned} \quad (4-48)$$

where the first row of right hand side of Eq. (4-48) shows the displacement of origin from \mathbf{O} to \mathbf{Y} . Then, the first term of the second row is rewritten to that of the third row by using Eq. (4-45). The superscript \mathbf{O} is explicitly attached to stress the origin before the displacement. The transformation from the second term of the second row of Eq. (4-48) to that of the third row was made by using Eq. (2-28). There is no specification of the origin, \mathbf{O} or \mathbf{Y} , since the value of $\frac{\partial \mu^N}{\partial X}$ is not depend on the origin of the coordinate as proved in Eq. (4-33).

Next we will consider the electronic part of the magnetic dipole moment of Eq. (2-27), \mathbf{m}^{el} , which can be written as

$$\mathbf{m}^{\text{el}} = -\frac{1}{2c} \sum_a e (\mathbf{X}_a \times \dot{\mathbf{X}}_a). \quad (4-49)$$

The magnetic dipole moment for the displacement of the origin as much as \mathbf{Y} is written as

$$\begin{aligned} (\mathbf{m}^{\text{el}})^Y &= -\frac{1}{2c} \sum_a e \left((\mathbf{X}_a - \mathbf{Y}) \times \frac{\partial}{\partial t} (\mathbf{X}_a - \mathbf{Y}) \right) \\ &= (\mathbf{m}^{\text{el}})^O + \frac{1}{2c} \sum_a e (\mathbf{Y} \times \dot{\mathbf{X}}_a) \\ &= (\mathbf{m}^{\text{el}})^O + \frac{e}{2mc} \sum_a (\mathbf{Y} \times \mathbf{P}_a), \end{aligned} \quad (4-50)$$

where \mathbf{P}_a is the momentum of the a th electron. Eq. (4-50) is equally written as

$$(\mathbf{m}_\alpha^{\text{el}})^Y = (\mathbf{m}_\alpha^{\text{el}})^O + \frac{e}{2mc} \epsilon_{\alpha\beta\gamma} \sum_a Y_\beta P_{a\gamma}. \quad (4-51)$$

Substituting this into Eq. (4-47), we can obtain

$$\begin{aligned}
 \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^Y &= -2i\hbar \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | (m_\alpha^{\text{el}})^0 + \frac{e}{2mc} \epsilon_{\alpha\beta\gamma} \sum_a Y_\beta P_{a\gamma} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2} \\
 &= \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 - \frac{ie\hbar}{mc} \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | \epsilon_{\alpha\beta\gamma} \sum_a Y_\beta P_{a\gamma} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2} \\
 &= \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 - \frac{ie\hbar}{mc} \epsilon_{\alpha\beta\gamma} Y_\beta \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | \sum_a P_{a\gamma} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2}.
 \end{aligned} \tag{4-52}$$

Taking the next relation,

$$\langle \Psi_s^0 | P_{a\gamma} | \Psi_n^0 \rangle = -\frac{im}{\hbar} (E_n^0 - E_s^0) \langle \Psi_s^0 | X_{a\gamma} | \Psi_n^0 \rangle, \tag{4-53}$$

into consideration, Eq. (4-52) can be rewritten as

$$\begin{aligned}
 &\left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^Y \\
 &= \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 - \frac{ie\hbar}{mc} \epsilon_{\alpha\beta\gamma} Y_\beta \sum_{n \neq s} \frac{-\frac{im}{\hbar} (E_n^0 - E_s^0) \langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | \sum_a X_{a\gamma} | \Psi_n^0 \rangle}{(E_s^0 - E_n^0)^2} \\
 &= \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 + \frac{1}{c} \epsilon_{\alpha\beta\gamma} Y_\beta \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | \sum_a eX_{a\gamma} | \Psi_n^0 \rangle}{E_s^0 - E_n^0} \\
 &= \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 - \frac{1}{c} \epsilon_{\alpha\beta\gamma} Y_\beta \sum_{n \neq s} \frac{\langle \Psi_n^0 | \frac{\partial H}{\partial X_{A\chi}} | \Psi_s^0 \rangle \langle \Psi_s^0 | \mu_\gamma^{\text{el}} | \Psi_n^0 \rangle}{E_s^0 - E_n^0}.
 \end{aligned} \tag{4-54}$$

By comparing Eq. (4-54) with Eq. (4-39), we can get

$$\left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^Y = \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{A\chi}} \right)^0 - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma^{\text{el}}}{\partial X_{A\chi}}. \tag{4-55}$$

Now we could derive the expressions of two parts of AAT for the origin displacement, that is, the nuclear part in Eq. (4-48) and the electronic part in Eq. (4-55). Combining these two equations, the next relation can be obtained,

$$\begin{aligned}
\left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^Y &= \left(\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}}\right)^Y + \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{Ax}}\right)^Y \\
&= \left\{ \left(\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}}\right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma^N}{\partial X_{Ax}} \right\} + \left\{ \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{Ax}}\right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma^{\text{el}}}{\partial X_{Ax}} \right\} \\
&= \left\{ \left(\frac{\partial m_\alpha^N}{\partial \dot{X}_{Ax}}\right)^O + \left(\frac{\partial m_\alpha^{\text{el}}}{\partial \dot{X}_{Ax}}\right)^O \right\} - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \left(\frac{\partial \mu_\gamma^N}{\partial X_{Ax}} + \frac{\partial \mu_\gamma^{\text{el}}}{\partial X_{Ax}} \right) \\
&= \left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma}{\partial X_{Ax}}. \tag{4-56}
\end{aligned}$$

To investigate the origin dependence of the rotational strength, we must obtain the formula for derivatives of the magnetic dipole moment by momentum in normal coordinate space. This will be done by the substitution of the variables in Eq. (4-56) by the corresponding ones in normal coordinate as

$$\begin{aligned}
\left(\frac{\partial m_\alpha}{\partial P_k}\right)^Y &= \sum_A \sum_X \left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^Y \cdot \frac{\partial \dot{X}_{Ax}}{\partial P_k} \\
&= \sum_A \sum_X \left\{ \left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma}{\partial X_{Ax}} \right\} \cdot \frac{\partial \dot{X}_{Ax}}{\partial P_k} \\
&= \sum_A \sum_X \left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^O \cdot \frac{\partial \dot{X}_{Ax}}{\partial P_k} - \frac{1}{2c} \sum_A \sum_X \epsilon_{\alpha\beta\gamma} Y_\beta \left(\frac{\partial \mu_\gamma}{\partial X_{Ax}} \cdot \frac{\partial \dot{X}_{Ax}}{\partial Q_k} \right) \\
&= \left(\frac{\partial m_\alpha}{\partial P_k}\right)^O - \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_\beta \frac{\partial \mu_\gamma}{\partial Q_k}. \tag{4-57}
\end{aligned}$$

The vector expression of the above equation is

$$\left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^Y = \left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^O - \frac{1}{2c} \left(\mathbf{Y} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right) \right). \tag{4-58}$$

Thus, using Eqs. (4-44) and (4-58), the rotational strength for k th normal mode, that is Eq. (2-23), is given as

$$\begin{aligned}
\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right) \cdot \left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^Y &= \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right) \cdot \left\{ \left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^O - \frac{1}{2c} \left(\mathbf{Y} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right) \right) \right\} \\
&= \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right) \cdot \left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^O - \frac{1}{2c} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right) \cdot \left(\mathbf{Y} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right) \right) \\
&= \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right) \cdot \left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^O. \tag{4-59}
\end{aligned}$$

For the sake of simplicity, the coefficient, $\hbar/2$, is omitted. The second term in the second row in Eq. (4-59) becomes zero according to the rule of scalar triple product.

Notice that \mathbf{Y} is the coordinate after the arbitrary displacement from the original position \mathbf{O} , and \mathbf{O} can be set freely at any point. The Eq. (4-59) tells us the values of the two rotational strengths which include $\left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^{\mathbf{Y}}$ and $\left(\frac{\partial \mathbf{m}}{\partial P_k}\right)^{\mathbf{O}}$ terms are the same regardless of the different origins. This means that the rotational strength for k th normal mode does not depend on the molecular origin.

So far we have chosen the same \mathbf{Y} for all the nuclei of a molecule. We will choose the specific origin Y_A for each nucleus A hereafter. Then, through the similar procedure, the analogous expression to Eq. (4-56) can be given as

$$\left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^{\mathbf{O}} = \left(\frac{\partial m_\alpha}{\partial \dot{X}_{Ax}}\right)^{Y_A} + \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_{A\beta} \left(\frac{\partial \mu_\gamma}{\partial X_{Ax}}\right)^{Y_A}. \quad (4-60)$$

Let us define $\left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A$ and $\left(\frac{\partial m_\alpha}{\partial P_k}\right)_A$ as follows,

$$\left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A = \sum_x \frac{\partial \mu_\alpha}{\partial X_{Ax}} \cdot \frac{\partial X_{Ax}}{\partial Q_k}, \quad (4-61)$$

$$\left(\frac{\partial m_\alpha}{\partial P_k}\right)_A = \sum_x \frac{\partial m_\alpha}{\partial \dot{X}_{Ax}} \cdot \frac{\partial \dot{X}_{Ax}}{\partial P_k}, \quad (4-62)$$

where $A = A, B, C, \dots$, specifying the different atoms, and x is $x, y,$ or z . The superscript \mathbf{O} or Y_A is omitted for the derivatives since these formulae can be applied independently of the choice of the origin.

In the same way as the case of common origin as a whole molecule, the relation analogous to Eq. (4-44) can be derived for the arbitrary displacement of each atom as follows,

$$\left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A^{\mathbf{O}} = \left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A^{Y_A}. \quad (4-63)$$

Substituting Eq. (4-60) into Eq. (4-62), that is assuming the origin of the Eq. (4-62) to be \mathbf{O} , we can get

$$\begin{aligned}
\left(\frac{\partial m_\alpha}{\partial P_k}\right)_A^0 &= \sum_x \left(\frac{\partial m_\alpha}{\partial \dot{X}_{\Lambda X}}\right)^0 \cdot \frac{\partial \dot{X}_{\Lambda X}}{\partial P_k} \\
&= \sum_x \left(\left(\frac{\partial m_\alpha}{\partial \dot{X}_{\Lambda X}}\right)^{Y_A} + \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_{\Lambda\beta} \left(\frac{\partial \mu_\gamma}{\partial X_{\Lambda X}}\right)^{Y_A} \right) \cdot \frac{\partial \dot{X}_{\Lambda X}}{\partial P_k} \\
&= \left(\frac{\partial m_\alpha}{\partial P_k}\right)_A^{Y_A} + \sum_x \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_{\Lambda\beta} \left(\frac{\partial \mu_\gamma}{\partial X_{\Lambda X}}\right)^{Y_A} \cdot \frac{\partial \dot{X}_{\Lambda X}}{\partial Q_k} \\
&= \left(\frac{\partial m_\alpha}{\partial P_k}\right)_A^{Y_A} + \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_{\Lambda\beta} \sum_x \left(\frac{\partial \mu_\gamma}{\partial X_{\Lambda X}}\right)^{Y_A} \cdot \frac{\partial X_{\Lambda X}}{\partial Q_k} \\
&= \left(\frac{\partial m_\alpha}{\partial P_k}\right)_A^{Y_A} + \frac{1}{2c} \epsilon_{\alpha\beta\gamma} Y_{\Lambda\beta} \left(\frac{\partial \mu_\gamma}{\partial Q_k}\right)_A^{Y_A}.
\end{aligned} \tag{4-64}$$

Then, from Eqs. (4-63) and (4-64),

$$\begin{aligned}
&\left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)^0 \cdot \left(\frac{\partial m_\alpha}{\partial P_k}\right)^0 \\
&= \sum_A \left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A^0 \cdot \sum_{A'} \left(\frac{\partial m_\alpha}{\partial P_k}\right)_{A'}^0 \\
&= \sum_A \sum_{A'} \left\{ \left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A^{Y_A} \cdot \left(\frac{\partial m_\alpha}{\partial P_k}\right)_{A'}^{Y_{A'}} + \frac{1}{2c} \left(\frac{\partial \mu_\alpha}{\partial Q_k}\right)_A^{Y_A} \cdot \left(\epsilon_{\alpha\beta\gamma} Y_{A'\beta} \left(\frac{\partial \mu_\gamma}{\partial Q_k}\right)_{A'}^{Y_{A'}} \right) \right\}.
\end{aligned} \tag{4-65}$$

This is rewritten in vector expression as

$$\begin{aligned}
\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)^0 \cdot \left(\frac{\partial \mathbf{m}}{\partial \mathbf{P}_k}\right)^0 &= \sum_A \sum_{A'} \left\{ \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \cdot \left(\frac{\partial \mathbf{m}}{\partial \mathbf{P}_k}\right)_{A'}^{Y_{A'}} + \frac{1}{2c} \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \cdot \left(\mathbf{Y}_{A'} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \right) \right\} \\
&= \sum_A \sum_{A'} \left\{ \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \cdot \left(\frac{\partial \mathbf{m}}{\partial \mathbf{P}_k}\right)_{A'}^{Y_{A'}} + \frac{1}{2c} \mathbf{Y}_{A'} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \right) \right\}.
\end{aligned} \tag{4-66}$$

Let us define the vector $\mathbf{Y}_{A'A}$ as follows,

$$\mathbf{Y}_{A'A} = \mathbf{Y}_{A'} - \mathbf{Y}_A. \tag{4-67}$$

Then the second term of the right hand side of Eq. (4-66) can be written as

$$\begin{aligned}
&\sum_A \sum_{A'} \frac{1}{2c} \mathbf{Y}_{A'} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \right) \\
&= \sum_A \sum_{A'} \frac{1}{2c} (\mathbf{Y}_A + \mathbf{Y}_{A'A}) \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \right) \\
&= -\sum_A \sum_{A'} \left\{ \frac{1}{2c} \mathbf{Y}_A \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \right) \right\} + \sum_A \sum_{A'} \frac{1}{2c} \mathbf{Y}_{A'A} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{Q}_k}\right)_A^{Y_A} \right).
\end{aligned} \tag{4-68}$$

Noticing the numerical relation as shown below,

$$\sum_A \sum_{A'} \left\{ \frac{1}{2c} \mathbf{Y}_A \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_{A'}^{Y_{A'}} \right) \right\} = \sum_A \sum_{A'} \left\{ \frac{1}{2c} \mathbf{Y}_{A'} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \right) \right\}, \quad (4-69)$$

we know that the value of the term in the left hand side of Eq. (4-68) is the same as that of the first term in the third row. Then, the following relation can be obtained,

$$\sum_A \sum_{A'} \frac{1}{2c} \mathbf{Y}_{A'} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \right) = \sum_A \sum_{A'} \frac{1}{4c} \mathbf{Y}_{A'A} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \right). \quad (4-70)$$

Substituting this into Eq. (4-67), we can get

$$\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)^0 \cdot \left(\frac{\partial \mathbf{m}}{\partial P_k} \right)^0 = \sum_A \sum_{A'} \left\{ \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \cdot \left(\frac{\partial \mathbf{m}}{\partial P_k} \right)_{A'}^{Y_{A'}} + \frac{1}{4c} \mathbf{Y}_{A'A} \cdot \left(\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_{A'}^{Y_{A'}} \times \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_A^{Y_A} \right) \right\}. \quad (4-71)$$

The specific origin \mathbf{Y}_A for each atom is arbitrary, and the molecular origin \mathbf{O} can be set freely at anywhere. Therefore, the rotational strength for k th normal mode expressed as Eq. (4-71) is independent of the molecular origin \mathbf{O} . The specific origin \mathbf{Y}_A for each atom is called the distributed origin, and the gauge used in Eq. (4-71) is called the distributed origin gauge¹¹⁾.

The rotational strengths calculated in this way are independent of the molecular origin \mathbf{O} . However, we assumed that the accurate wavefunctions were used to evaluate the physical quantities included in Eq. (4-71). Therefore, the calculated value of rotational strength given by Eq. (4-71) is independent of the origin only for the exact wavefunctions and for the approximate wavefunctions expanded in a complete one-electron basis function because Eq. (4-53) holds only with the accurate wavefunctions^{10), 11)}. In practice, only the finite basis sets are available, and the calculations are not necessarily gauge independent. One of the solution for this problem has been proposed by Bak et al.¹⁰⁾. They used the gauge-invariant atomic orbitals (GIAO), which were introduced by London to calculate the magnetic properties¹²⁾.

The Hamiltonian for one-electron, one-nucleus system in the presence of external magnetic field can be expressed as

$$H = \frac{1}{2} (-i\nabla + \mathbf{A})^2 - \frac{eZ}{|\mathbf{r} - \mathbf{R}|}, \quad (4-72)$$

where eZ and \mathbf{R} are the charge and the position of the nucleus, and \mathbf{r} is the position of the electron. \mathbf{A} is the magnetic vector potential, defined as

$$\mathbf{A} = \frac{1}{2} (\mathbf{B} \times (\mathbf{r} - \mathbf{O})), \quad (4-73)$$

where \mathbf{B} is the external magnetic field, and \mathbf{O} is the gauge origin.

Let us define the Hamiltonian of the system in the absence of external magnetic field as H_0 . Then the Schrödinger equation can be written as

$$H_0\chi_n = E_n\chi_n, \quad (4-74)$$

where χ_n is the n th atomic orbital. Then the n th GIAO, ω_n , can be obtained by multiplying χ_n with a phase factor,

$$\omega_n = \exp(-i\mathbf{A}_N^e \cdot \mathbf{r})\chi_n, \quad (4-75)$$

where

$$\mathbf{A}_N^e = \frac{1}{2}(\mathbf{B} \times (\mathbf{R} - \mathbf{O})). \quad (4-76)$$

Bak et al. have done multiconfigurational self-consistent-field calculations using these GIAOs, and derived the same expression as Eq. (4-57) for the exact wavefunctions, and then, the gauge-origin independent rotational strengths¹⁰⁾. This approach has a merit of converging faster with increasing size of the basis set used¹³⁾, and is preferably used for a computational method.

5. Application to VCD Spectrum of OH Bending Mode of (S)-(+)-2-Butanol

The molecular structure of (S)-(+)-2-butanol is shown in Fig.2. This molecule has four single bonds, and two of these, i.e. C²-C³ and C-O, can give rise to rotational isomerism. Around each bond may exist three stable conformations, and totally nine rotational isomers are possible. They are named by using two symbols as shown in Fig.3. The first large letters denote the dihedral angle between the OH and CH₃ group around the C²-C³ bond. The second small letters show the dihedral angle between H atom of OH group and C₂H₅ group around the C-O bond. The letter G or g means a gauche form and T or t means a trans form. The + and - signs represent the directions of the dihedral angle, where the + sign indicates the positive or anti-clockwise direction.

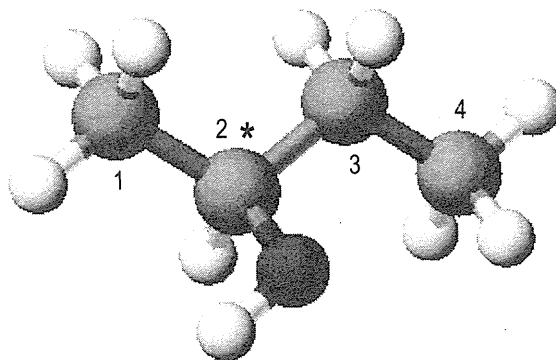


Fig.2 Structure of (S)-(+)-2-butanol
The symbol * denotes the chiral center.

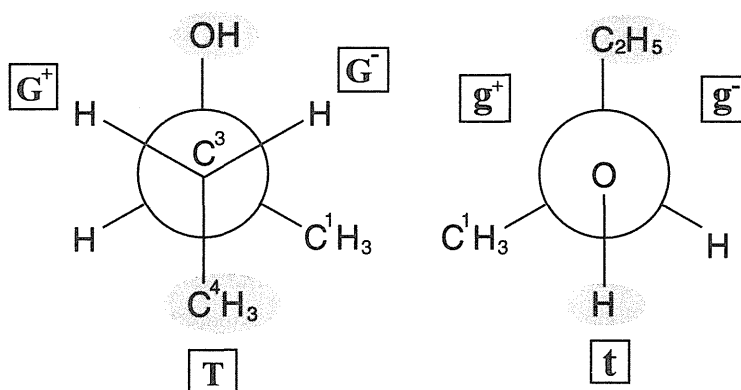


Fig.3 Rotational isomers of (S)-(+)-2-butanol

All nine conformers were geometry-optimized at B3LYP/6-31++G** level by using Gaussian 98¹⁴⁾ program package. All of them were converged, and from the total energies obtained the relative population as a free molecule at 300 K was estimated. This is shown in Table1. F. Wang et al.¹⁵⁾ estimated the relative population of 2-butanol based on Gibbs free energies obtained from the DFT calculation at a level of B3LYP/6-31G*. Their results are slightly different from ours, but agree fairly well as a whole. We also calculated the vibrational frequencies and intensities of both IR and VCD at B3LYP/6-31++G** level, and predicted the spectra.

Table 1 Relative population of each conformer at 300 K
The population were estimated according to the result of B3LYP/6-31++G** level calculation.

| conformer | total energy (hartree) | relative population (%) |
|-------------------------------|-----------------------------|------------------------------|
| G ⁺ t | -233.697904611 | 25.03 |
| G ⁺ g ⁻ | -233.697661925 | 19.39 |
| G ⁺ g ⁺ | -233.697502998 | 16.40 |
| Tg ⁻ | -233.697134819 | 11.13 |
| Tt | -233.697000712 | 9.67 |
| Tg ⁺ | -233.696759868 | 7.50 |
| G ⁻ g ⁻ | -233.696262279 | 4.44 |
| G ⁻ t | -233.696200339 | 4.16 |
| G ⁻ g ⁺ | -233.695624548 | 2.27 |

The measurements of IR and VCD spectra of (S)-(+)-2-butanol of neat sample and CS₂ solution of various concentrations from 1.0 M to 0.002 M have been done at room temperature. The IR and VCD spectra were recorded on a Fourier transform VCD spectrometer, Chiralir, constructed by Bomem-BioTools, with a ZnSe PEM and a BaF₂ polarizer. The spectral resolution was set to 4 cm⁻¹ and the measurement region was restricted to 2000-800 cm⁻¹ by using an optical filter transmitting below 2000 cm⁻¹. The spectrum was accumulated on the narrow band MCT detector cooled by liquid N₂. The accumulation time of VCD spectrum was 2 hours, with about 50 scans per minute. The path length of the liquid cell for VCD spectrum was adjusted from 15 μm to 1 mm for obtaining the proper absorbance of around 0.4 to get a good VCD signal. BaF₂ was used for the window material. (S)-(+)-2-butanol and CS₂ solvent were purchased from Aldrich Chemical Co., Inc. and were used without further purification. The purity of (S)-(+)-2-butanol was certified to 99 % and the enantiomeric excess was uncertain.

Also Ar matrix-isolated IR spectrum was measured. The temperature was set to 12 K, and the matrix-to-solute ratio was 2000.

Fig.4(a) shows the IR spectra of (S)-(+)-2-butanol at various concentrations. The second trace from the bottom is Ar matrix-isolated spectrum. The bottom trace is the calculated one, which is a combination of all nine conformers based on the relative populations obtained from the DFT method. The calculated frequencies are scaled by 0.985. As is seen here, the neat spectrum does not agree well with the calculated one. This is quite natural because the neat spectrum reflects the intermolecular hydrogen bonding, while the calculated one is constructed based on free molecules. However, in

dilute solutions, the spectra differ from the neat spectrum and some new peaks appear. The further diluted spectrum looks more like the calculated one. This is because that dissolving the sample in the solvent makes molecules more free from the intermolecular hydrogen bonding. Furthermore, the dilute IR spectra below 0.1 M do not change anymore, and also agree very well with the Ar matrix-isolated one. Additionally, the appearances of them do not depend on the kinds of solvents. (See Fig.5.) From these evidences, the molecules in solution below 0.1 M can be assumed to exist almost completely free from the intermolecular hydrogen bonding. These facts mean that the calculations we did are reliable, and every observed peak can be assigned by comparing with the calculated spectrum.

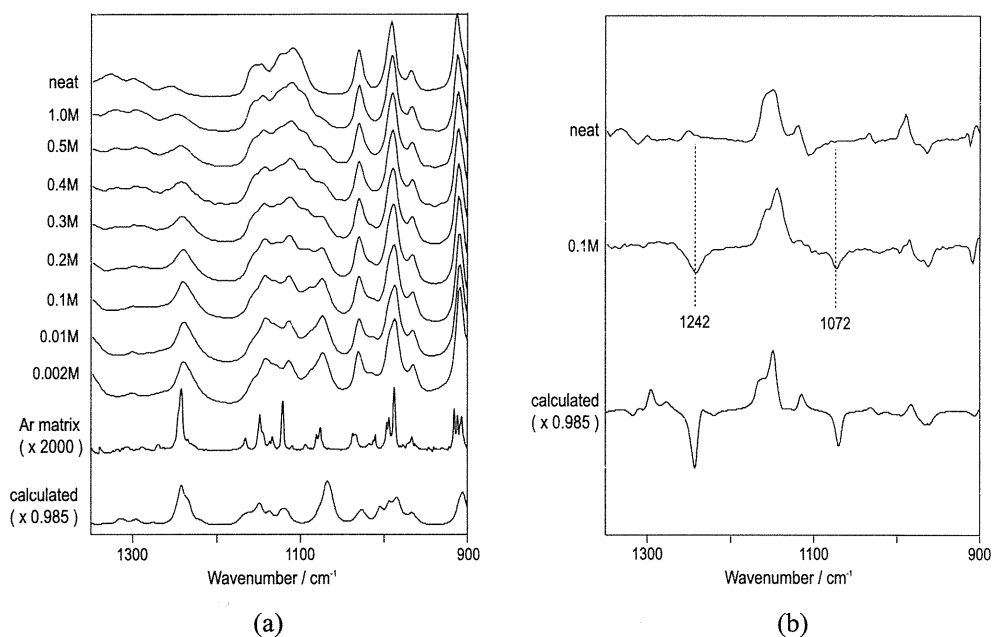


Fig.4 (a) IR and (b) VCD spectra of (S)-(+)-2-butanol at various concentrations CS₂ was used as a solvent. The bottom traces are calculated spectra. The frequencies are scaled by 0.985.

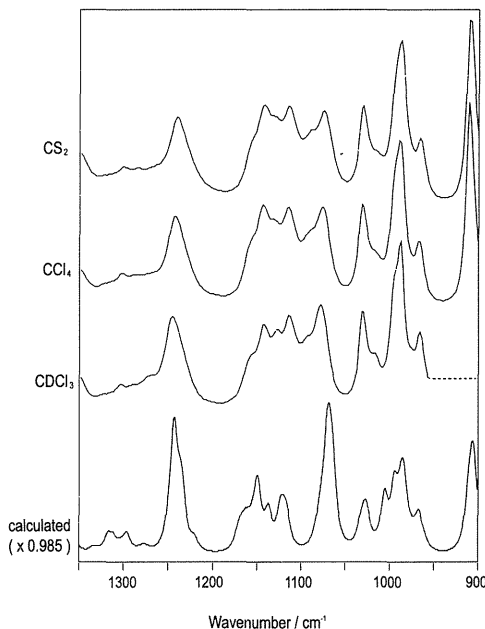


Fig.5 IR spectra of 2-butanol in 0.1 M solution of various solvents
No data were obtained below 950 cm^{-1} in CDCl_3 solution because of the strong absorption of the solvent.

Fig.4(b) shows the VCD spectra of (*S*)-(+)-2-butanol. The top trace is the observed spectra of neat sample, and the second trace is of 0.1 M CS_2 solution. The baselines are corrected by subtracting the averaged spectrum of (*R*)- and (*S*)- enantiomers. The bottom trace is the calculated one. It is a combination of all nine conformers, which corresponds to the above-mentioned calculated IR spectrum, and the frequencies are also scaled by 0.985. In 0.1 M VCD spectrum, two peaks at 1242 cm^{-1} and 1072 cm^{-1} have strong intensities. It is impossible to recognize both bands in neat spectrum. Comparing with the calculated spectrum, these bands can be assigned to OH bending mode mixed with some other vibrational modes; the 1242 cm^{-1} band is CH_3 (and/or CH_2 and/or CH) deformation mixed with OH bending, and the 1072 cm^{-1} band is OH bending mixed with the skeletal stretching. This phenomenon, that the VCD bands of OH bending mode appear strongly in dilute solution, is the same as in the cases of 1-amino-2-propanol and some other alcohol molecules, as was found in our previous studies^{3), 16)}. This is noteworthy because it suggests that the OH bending band might give us some new valuable information.

When people discuss about hydrogen bonding system, they generally talk about OH stretching mode, not about OH bending mode. The OH bending mode has never been

considered as a source of useful information¹⁷⁾, and has been ignored in most cases. This is due to the facts that the IR band of OH bending mode is not very strong in general, and also the mixing with many other vibrational modes makes the analyses rather difficult. However, a joint measurement and analysis of VCD and IR spectra might allow the OH bending band to afford some valuable information, especially about the molecular structures of hydrogen bonding systems. In other words, since OH stretching band provides a piece of information along the OH axis direction, while the OH bending band provides a piece of information along the direction perpendicular to that axis, they might give us some information about the three-dimensional structure of hydrogen bonding system.

There is another characteristic feature about the spectra of 2-butanol. Fig.6(a) and (b) show the calculated IR and VCD spectra of each conformer, respectively. The top traces are the combination of all nine conformers. The frequencies of spectra here are not scaled. The mode assignment is complicated for a molecule of this size. However, we can pick up the bands which have a contribution of OH bending mode judging on the potential energy distribution. We assigned two bands of the OH bending characteristic in each spectrum. They are shaded as shown in Fig.6. The higher frequency bands correspond to observed 1242 cm^{-1} band, and lower ones correspond to 1072 cm^{-1} band. From these figures, we can classify these OH bending bands into three types according to the conformation of OH group. As for g^- form, the intensities of IR bands corresponding to 1242 cm^{-1} band are strong, and VCD bands are negative and strong. The intensities of IR bands corresponding to 1072 cm^{-1} band are weak, and VCD bands are almost inactive. In these conformers with g^- form, the OH bending mode mainly contributes to 1242 cm^{-1} band. As for g^+ form, the intensities of IR bands corresponding to 1242 cm^{-1} band are very weak, and VCD bands are positive and middle. The intensities of IR bands corresponding to 1072 cm^{-1} band are strong, and VCD bands are negative and strong. In these conformers with g^+ form, the OH bending mode mainly contributes to 1072 cm^{-1} band. As for t form, the intensities of IR bands corresponding to 1242 cm^{-1} band are middle, and VCD bands are almost inactive. The intensities of IR bands corresponding to 1072 cm^{-1} band are also middle, and VCD bands are weak. In these conformers with t form, the OH bending mode contributes to both 1242 cm^{-1} and 1072 cm^{-1} almost equally. The statements so far made are summarized in Table 2. As is shown in the table, the IR and VCD characteristics do not depend on the CCCO torsion angle, G or T. In other words, the characteristics of this molecule is governed only by the relative configuration between the OH group and the rest part of the molecule, and not affected by the structure of alkyl skeleton.

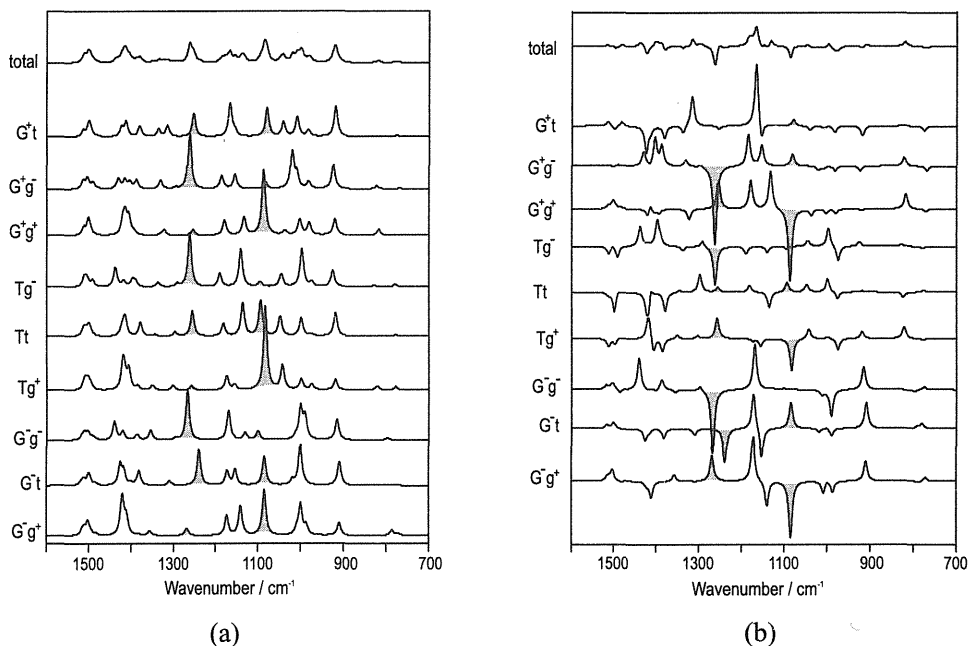


Fig.6 Calculated spectra of (S)-(+)-2-butanol : (a) IR (b) VCD
Calculation was carried out at B3LYP/6-31++G** level.

Table 2 Classification of OH bending bands of 2-butanol

| | | ~1242cm ⁻¹ | | ~1072cm ⁻¹ | |
|----------------|-----|-----------------------|-----|-----------------------|--|
| g ⁻ | IR | strong | IR | weak | |
| | VCD | negative, strong | VCD | almost inactive | |
| g ⁺ | IR | weak | IR | strong | |
| | VCD | positive, middle | VCD | negative, strong | |
| t | IR | middle | IR | middle | |
| | VCD | almost inactive | VCD | positive, weak | |

We have made a semi-empirical model to explain this feature described above. In the case of 2-butanol, the OH bending mode always splits into two bands. This is because OH bending mode is coupled with some other vibrational modes. Here, we have chosen the dynamic polarization (DP) model²⁾, which is an extension of the CO model. In this model, a molecule is divided into some parts, and the electric dipole moment derivative caused in one part is assumed to induce electric dipole moments in

surrounding parts. The electric dipole moment derivative and the induced electric dipole moment derivative are treated as a coupled oscillator. Two parameters are required in this model, one is the angle and the other is the distance, between the two electric dipole moment derivatives. We can expect the greater rotational strength when the angle is closer to 90 degrees and also when the distance is smaller. We have applied this model to the case of (S)-(+)-2-butanol.

We divide the molecule into two parts, the OH group and the rest, and assume the electric dipole moment derivatives localized on these two parts. One is accompanying the OH bending vibration, and the other is the one induced in the rest part of the molecule by the OH bending motion. Let us write these electric dipole moment derivatives as $\frac{\partial \mu_1}{\partial Q}$ and $\frac{\partial \mu_2}{\partial Q}$, respectively. According to the DP model, we can obtain

the stronger VCD signal when $\frac{\partial \mu_1}{\partial Q}$ and $\frac{\partial \mu_2}{\partial Q}$ lie more perpendicularly, and also more closely. Since $\frac{\partial \mu_2}{\partial Q}$ mostly depends on the electric dipole moment induced in C₂H₅

group, its direction can be assumed to be approximately along the C₂H₅ axis. Fig.7 shows each conformer looked from the direction along the O-H axis. The left column contains the conformers with g⁻ form, the middle with g⁺ form, and the right with t form. The top row contains the conformers with G⁺ skeleton, the middle with G⁻, and the bottom with T. As for g⁻ conformers, the molecules with G⁺ and G⁻ skeletons have $\frac{\partial \mu_1}{\partial Q}$ and $\frac{\partial \mu_2}{\partial Q}$ almost perpendicularly to each other. These aspects explain very well the observed VCD spectra, which have strong OH bending band. Although the molecules with T skeleton seem to have two electric dipole moment derivatives, $\frac{\partial \mu_1}{\partial Q}$ and $\frac{\partial \mu_2}{\partial Q}$, in parallel, they show rather strong VCD bands assignable to OH bending

against the prediction of weak intensity. It is impossible to explain the apparent contradictory phenomena with respect to the DP model with only two parameters, angle and distance. More input parameters seem to be required to resolve these problems. The same discussion can be approved about g⁺ conformers. As for t conformers, the angles between $\frac{\partial \mu_1}{\partial Q}$ and $\frac{\partial \mu_2}{\partial Q}$ are not so apart from 90 degrees, and

this predicts strong VCD signal contrary to the rather weak intensity. However, the distance between the two electric dipole moment derivatives is large in t conformers, and the effects of the distance might be stronger about this form. Thus, our model based on the DP model explains the relation between the VCD spectrum and the molecular structure very well as a whole.

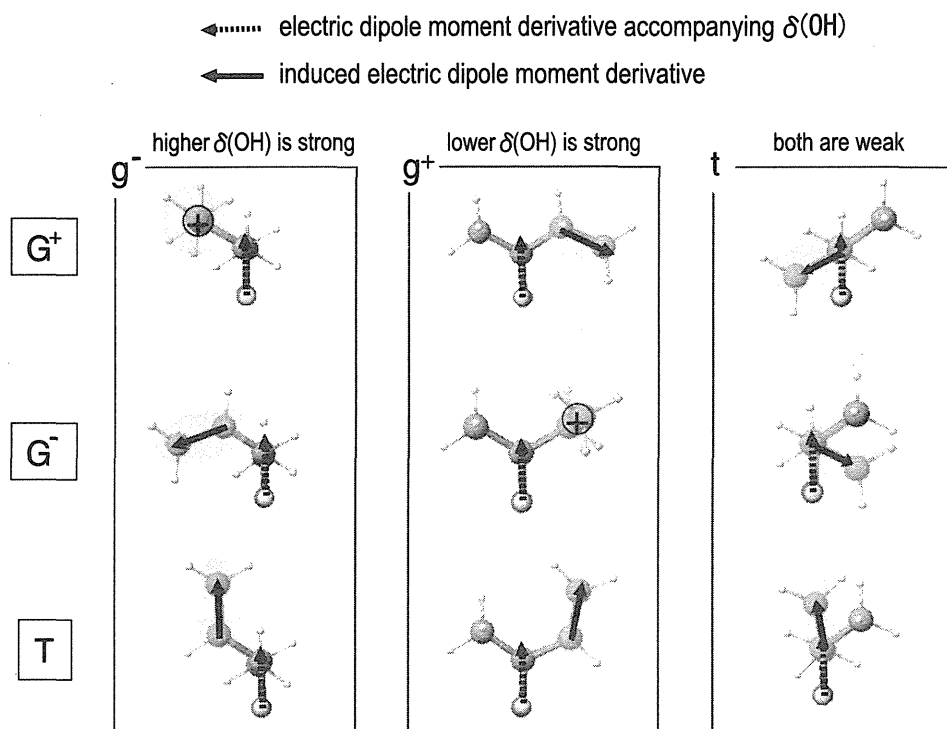


Fig.7 Electric dipole moment derivatives accompanying OH bending mode

To verify this model, we did the same kind of calculations and measurements about (S)-(+)-2-pentanol. Fig.8 shows the structure of (S)-(+)-2-pentanol. In the case of this molecule, we must consider C^3-C^4 torsional angle, and totally 27 rotational isomers may be possible. We named them as are shown in Fig.9. The first large letters denote the conformation of C^5H_3 group, and the latter two follow the same rule as the case of (S)-(+)-2-butanol.

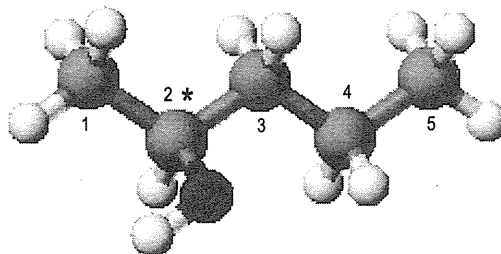


Fig.8 Structure of (S)-(+)-2-pentanol
The symbol * denotes the chiral center.

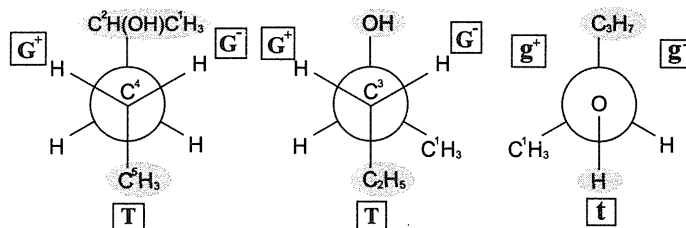


Fig.9 Rotational isomers of (S)-(+)-2-pentanol

Fig.10(a) and (b) show the IR and VCD spectra of (S)-(+)-2-pentanol at various concentrations, respectively. The baselines of VCD spectra are corrected by subtracting the averaged spectrum of (R)- and (S)- enantiomers. The bottom traces are the calculated ones composed of all 27 conformers according to the populations obtained from the DFT calculation at B3LYP/6-31++G** level. The frequencies are scaled by 0.985. As in the case of 2-butanol, the IR spectra below 0.1 M do not change anymore, and both IR and VCD spectra of dilute solution agree very well with the calculated ones, and the calculation can be trusted. Then Fig.11(a) and (b) are the calculated IR and VCD spectra of nine major conformers, respectively. The frequencies are not scaled. The bands of large contribution of OH bending mode are shaded. As seen here, the IR and VCD spectra of g^- and t conformers hold the same characteristic features as those of (S)-(+)-2-butanol. This fact ensures the model that we have mentioned above. However, the VCD spectra of g^+ conformers expresses the different aspects from those of (S)-(+)-2-butanol. The OH bending VCD bands, especially the lower frequency ones, of g^+ conformers of (S)-(+)-2-butanol show very strong intensities, but the corresponding bands of g^+ conformers of (S)-(+)-2-pentanol are very weak or almost inactive. The same feature is possessed by other 18 conformers of (S)-(+)-2-pentanol. At present, it is impossible to explain this feature by using the above-mentioned model. Probably it requires more parameters other than angle or distance. The difference of molecular structure may cause the scheme of the mode coupling different, resulting in the quite different appearances of IR and VCD bands. The effects of the distant groups might also not be negligible. We are upgrading our model in such viewpoints, and discuss the result in future publication.

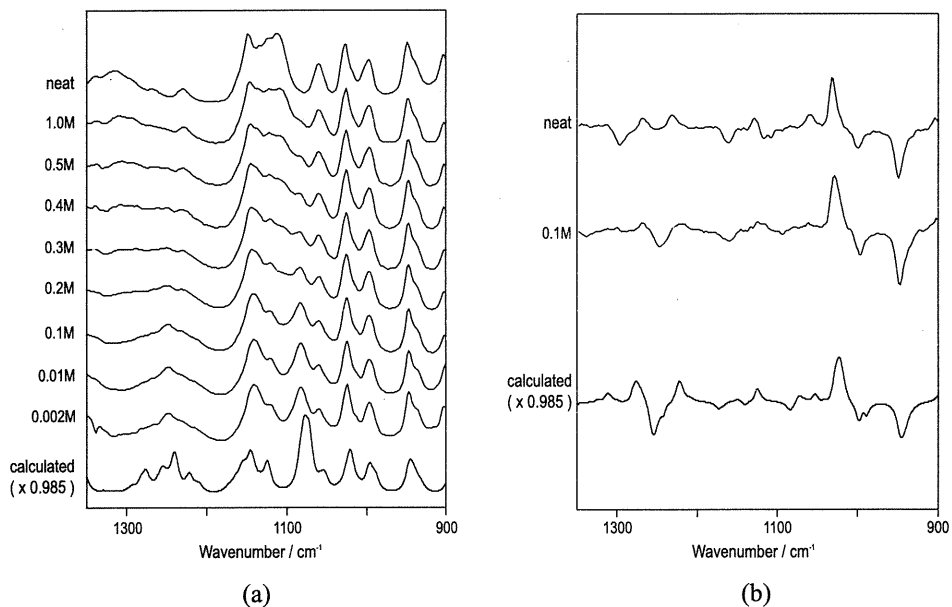


Fig.10 (a) IR and (b) VCD spectra of (S)-(+)-2-pentanol at various concentrations CS₂ was used as a solvent. The bottom traces are calculated spectra. The frequencies are scaled by 0.985.

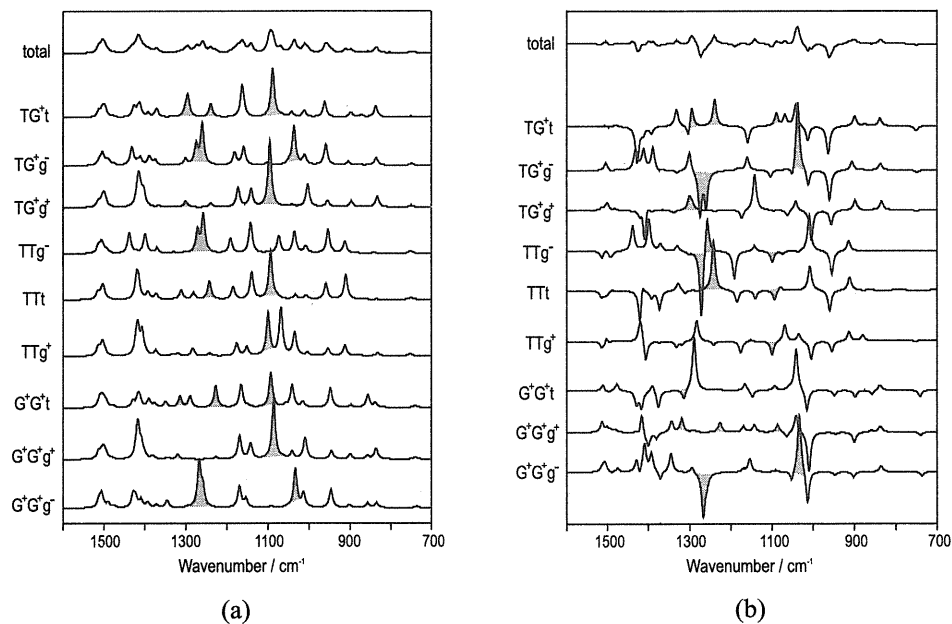


Fig.11 Calculated spectra of (S)-(+)-2-pentanol : (a) IR (b) VCD
Calculation was carried out at B3LYP/6-31++G** level.

6. Acknowledgement

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