

Vibrational Circular Dichroism Spectroscopy —Raman Optical Activity—

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振動円偏光二色性分光法 —Raman 光学活性—

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要 旨

著者らは円偏光赤外線を用いた二色性の分光により、光学活性分子の測定と解析を行ってきた。これまで、アルコール類の分子の場合には、無極性あるいは極性の弱い溶媒中に希釈することにより、分子間水素結合を遮断したスペクトルを観測でき、溶液状態での分子構造の研究にはほとんど情報をもたらさないと信じられてきたOH変角振動が振動円偏光二色性 (VCD) スペクトルには強い信号となって現れること、その信号の強度や符号が振動モードの観点から解釈できる可能性のあることを示してきた。生体分子の系に振動分光の研究を応用する場合、赤外分光とともにそれに相補的なRaman分光法が有用であることは、多くの研究例によって明らかである。光学活性分子の振動円偏光二色性分光ではROAと呼ばれる分光法がVCDに相補的な分光法ということになる。著者らの研究室では、本年度にこのROA分光装置を導入することになった。そこでこの際、Raman分光法の一般的な原理とROAの理論の概観を行い、導入したROA分光装置でどの程度のスペクトルが測定できるかを検討し、VCDとの比較を行うことにした。この論文はこれらの測定実験の予備的な結果を報告し、将来への理論あるいは新しいモデル構築の基礎となるものとして執筆した。

ABSTRACT

We have carried over experimental measurements and analyses of optically active molecules by dichroism spectroscopy with circularly polarized infrared light. We discovered the OH bending modes of alcoholic molecules give fairly strong VCD (vibrational circular dichroism) signals when the molecules are dissolved in nonpolar solvent or in solvent of weak polarity where intermolecular hydrogen bonding is shut off. The OH bending infrared band has been believed to be of low value in the study of molecular structure in liquid and in solution because of its weak absorption intensity. We have pointed out that the intensi-

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ties and signs of VCD signals including the OH bending band can be understood in terms of local vibrational modes and their relative arrangements, which seems to be of potential use not only for analysis of the spectrum but also for prediction of the spectrum of new molecule. It has been recognized through numerous researches that Raman spectroscopy complementary to infrared spectroscopy is useful in the study of biological molecules. The corresponding relation is a method called ROA (Raman optical activity) which is complementary to VCD spectroscopy in the study of optical active molecules. We have introduced an ROA spectrometer in 2003, which is the first commercially available apparatus in Japan. On this occasion, we review the general principle of Raman spectroscopy and its extension to ROA spectroscopy. We show some preliminary results of ROA measurement and compare the ROA spectra to the corresponding VCD spectra, and investigate the characteristic features of ROA spectra and applicability to optical active molecules, especially biological samples. This paper aims to be a basis for our future research of making a new model in interpreting VCD and ROA spectra, and for much complicated molecular systems.

I . Optical Activity

The different character of refractivity (n) and absorption coefficient (ϵ) of matters against left and right circularly polarized lights is called optical activity. Optical rotation is a phenomenon which rotates the plane of linear polarized light after the light passed a certain material or medium. The linear polarized light is considered to be the addition of left and right circularly polarized lights with the same amplitude and wavelength. When the speeds of the two circularly polarized lights (c/n) passing in a medium are different, there arises the phase difference between the two lights at the exit of the medium. In other word, polarized plane is rotated, and the degree of rotation of the polarization is called angle of rotation. When the rotation of the electric vector against time at a particular space point is clockwise if looked backward from the direction of propagation of light (or the trace of the electric vectors along the propagation coordinate at a particular time is right hand helix), the rotation is called dextrorotatory (d) or +, and when the rotation is anticlockwise, the levorotatory (l) or -. Quantitatively, the optical rotation angle α is defined as

$$\alpha = \frac{\pi}{\lambda} l (n^l - n^r), \quad 1-1)$$

where n^l and n^r are the refractive indices for left and right polarized lights, and λ is wavelength of the light and l is the path length (in dm) of the medium.

The phenomenon that the angle of rotation of optical active substance differs for its wavelength is called optical rotatory dispersion. The refractive index and absorption coefficients of optically active material are different for left and right circularly polarized lights. Since the refractive index is dependent on the wavelength, the angle of rotation varies for the wavelength. If there is any absorption of light, the incident linear polarized light turns out to be elliptically polarized light. In general, the optical rotatory dispersion is the mixture of the above-mentioned two phenomena.

When we detect the difference of the absorption coefficients of opposite circularly polarized lights, it is called as circular dichroism. Since the linear polarized light changes to elliptically polarized light, the circular dichroism is expressed not only by the difference of the absorption coefficients but also by ellipticity θ which is defined by $\tan \theta$ to be the ratio of the lengths of minor (short) axis against to major (long) axis.

These optical activities occur for a single crystal in which the molecular arrangement is in either real image or its mirror image. If a molecule itself has optical activity, its stereo structure is distinguished by either left-handed or right-handed geometry, that is the molecule has isomeric structures in real and its mirror images. One of these isomers is called an antipode or enantiomer, or optical isomer. In real organic compounds, the optical activity occurs for the molecule in which the four atoms or substituents connected to the central carbon atom are different. The carbon atom in above-mentioned position is called asymmetric carbon atom. The terminology described as chiral is also used for the nature where the two objects cannot be overlapped as the case of left-hand and right-hand. From the group theoretical point of view, the chiral nature is associated with the structure which has no rotatory-reflection symmetry. The asymmetric center is also expressed as chiral center.

Protein is an organic polymer which acts as the structural substance and as biofunctional substance in a living organism, and the protein is consisted of amino acid molecules which is mostly optical active or in fact they are exclusively of l-isomers except glycine (it is said there are some bacteria which have d-amino acids in the cell wall). Therefore, the detection of these chiral molecules is very important in the study of life mechanism from microscopic point of view.

Traditionally, electronic CD spectroscopy has been used in this field. Recently, however, the circular dichroism spectroscopy in molecular vibration field is rapidly developing because of availability of commercial apparatus and the theoretical calculation tools depending on high speed and large volumetric memory devices and sophisticated computer algorithm. We introduced a vibrational circular dichroism spectrometer using infrared absorption a few years ago. The vibrational circular dichroism spectrum in infrared region is specially called VCD (abbreviation of vibrational circular dichroism) spectrum. On the other hand, the complementary spectrum measured by Raman spectroscopy is referred to as (V) ROA (Raman optical activity) spectrum. We reviewed the fundamental theory of VCD spectroscopy and its spectra in our previous reports^{1,2)}. Here we review the basis of Raman spectroscopy and its ROA version, and show some of our preliminary experimental results.

II. Classical Theory of Raman Activity

Molecules are consisted of electrons with negative charge and nuclei with positive

charge. In non-polar molecules, the centers of positive and negative charges coincide with each other. On the other hand, in polar molecule the two centers are shifted each other. The degree of the shift of opposite charges is represented by electric dipole moment μ , as defined by

$$\mu_0 = \sum_i q_i r_i, \quad (2-1)$$

where the suffix 0 is used to represent the dipole moment under no external electric field. μ_0 is called permanent dipole moment, that is the charge distribution the molecule has intrinsically as its nature. μ is a vector, and its direction is defined to point from the negative to positive centers as shown in Fig. 1.

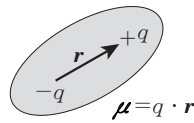


Fig.1 Definition of dipole moment

The dipole moment is defined to direct from negative to positive charges.

The charge distribution of the molecule exposed to the external electric field can be deviated from that of the molecule without the electric field. This phenomenon of charge redistribution is called polarization, and the electric dipole moment thus produced is called an induced (electric) dipole moment μ_p . This phenomenon is usually observed as the macroscopic phenomenon, such as dust adhesion on TV cathode ray tube or on intake tube of

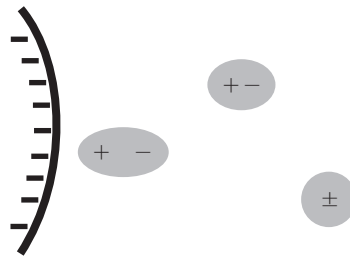


Fig.2 Polarization

Suppose certain material (say, TV screen) is negatively charged. In small particle with neutral charge such as a dust floating on the air, the center of positive charge is in coincident with that of negative charge. When the neutral particle approaches to the charged material, the two centers are separated. The positive center is closer to the charged material and the negative center is shifted to the other side. Because of the law of inverse square between charges, the attraction force prevail against the repulsive force, and the small particle (dust) adheres on the charged material (screen). The separation of the two centers is called polarization.

vacuum cleaner.

When the electric field \mathbf{E} is sufficiently low, the induced dipole moment is expressed as the first order expansion of \mathbf{E} , so that

$$\boldsymbol{\mu}_p = \alpha \mathbf{E}. \tag{2-2)}$$

The coefficient α is a second rank tensor which connects two vectors $\boldsymbol{\mu}_p$ and \mathbf{E} , and is called polarizability tensor. The explicit form for Cartesian coordinates is

$$\begin{pmatrix} (\mu_p)_x \\ (\mu_p)_y \\ (\mu_p)_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}. \tag{2-3)}$$

The equation 2-3) tells that the direction of the induced dipole moment is not necessarily aligned to the applied electric field, but can be declined as determined by the off-diagonal element of polarizability tensor. That means that the motion of an electron in the molecule is restricted by the molecular structure or by the other electrons in the molecule.

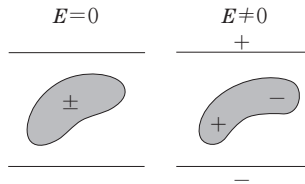


Fig.3 Polarizability

The magnitude of the induced dipole moment, $\boldsymbol{\mu}$, under applied external electric field, \mathbf{E} , is dependent on the polarizability, α , such that $\boldsymbol{\mu} = \alpha \mathbf{E}$. The direction of the induced dipole moment or the shift of charges is not necessarily along the applied field. Therefore, the polarizability is a tensor quantity.

Now we must consider the case of periodical electric field produced by the applied electromagnetic radiation (actually laser light) such as

$$\mathbf{E} = E_0 \cos 2\pi\nu_R t, \tag{2-4)}$$

where E_0 is the amplitude of the wave and ν_R is the frequency. In general, the molecule has several vibrational modes. Let take one of its modes with frequency of ν_M . Then the polarizability elements also should vibrate with the same frequency of the particular normal vibration Q . Here we take one of the elements as

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial Q} \cos 2\pi\nu_M t. \tag{2-5)}$$

Substituting 2-4) and 2-5) into 2-2), we obtain the following relation,

$$\begin{aligned}
 \mu_p &= \left(\alpha_0 + \frac{\partial \alpha}{\partial Q} \cos 2\pi \nu_M t \right) (E_0 \cos 2\pi \nu_R t) \\
 &= \alpha_0 E_0 \cos 2\pi \nu_R t \\
 &\quad + \frac{1}{2} \frac{\partial \alpha}{\partial Q} E_0 \cos 2\pi (\nu_R + \nu_M) t \\
 &\quad + \frac{1}{2} \frac{\partial \alpha}{\partial Q} E_0 \cos 2\pi (\nu_R - \nu_M) t.
 \end{aligned} \tag{2-6}$$

The oscillating electric charge, in our case the electric dipole moment, emits the electromagnetic radiation of the same oscillation frequency. Therefore, the equation 2-6) shows that there are three electromagnetic radiations different in frequencies are emitted. The first term in the rightmost equation denotes Rayleigh scattering, such that the scattered light has the same frequency as the incident laser light. In fact, Rayleigh scattering constitute most of the intensities of the scattered light. However, there are very weak components in the scattered light, weaker than 10^{-6} of the incident light strength. The frequencies are different from that of the incident light. This is called Raman scattering after the name C.V. Raman who discovered the phenomenon in 1928. This effect is described as the second and third terms in 2-6). This is essentially the same as beat frequency when the two waves of different frequencies are mixed up. The second term with sum frequency, $\nu_R + \nu_M$, corresponds to anti-Stokes scattering, and the third term with difference frequency, $\nu_R - \nu_M$, corresponds to Stokes scattering.

Equation 2-6) tells that the value of $\partial \alpha / \partial Q$ should be non-zero to obtain Raman activity. That means that the polarizability must vary for the particular vibration for Raman spectrum to be observable. Let's explain by taking CO₂ molecule as an example. We must remember that the frequency of excitation laser is much higher than the molecular vibrations, so that the molecule experiences more than 10 oscillations of exciting electromag-

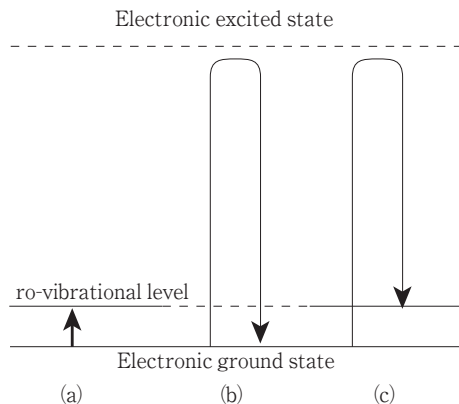


Fig.4 Rayleigh and Raman scattering

(a) Infrared absorption: direct transition from the ground level to the ro-vibrationally excited level within the ground electronic state. (b) Rayleigh scattering. (c) (Stokes-) Raman scattering.

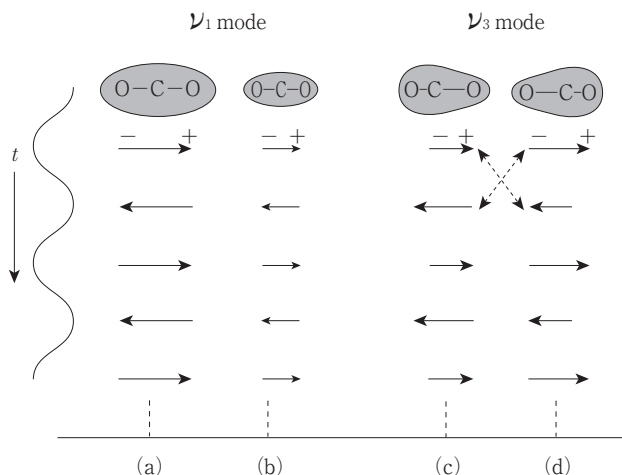


Fig.5 Visual image of Raman activity

In one cycle of molecular vibration, the molecule is affected by oscillating radiation field with more than one order higher frequency. The induced dipole moments in the course of molecular vibrations are shown with arrows. The resulting induced dipole moments are considered to be the average of (a) and (b) for ν_1 (totally symmetric stretching) mode, and (c) and (d) for ν_3 (anti-symmetric stretching) mode. For ν_3 mode, the induced dipole moments connected by dotted arrows, for example, cancel each other. Therefore, ν_3 mode is inactive in Raman spectrum.

netic waves which generates the induced dipole moment in one cycle of molecular vibration. Consider the anti-symmetric stretching vibration of CO₂. As shown in Fig.5 (c), the electron cloud of distorted molecule generates the oscillating induced dipole moment in frequency of exciting laser wave. On the other hand, as shown in Fig.5 (d), anti-symmetrically distorted molecule will generate induced dipole moment just in 180 degree out-of-phase to that shown in (c). The induced dipole moments shown in Fig.5 (c) and (d) cancel each other, and there is no net induced dipole moment. At the end, there is no scattered light from the sample molecule and this vibrational mode has no Raman activity. The magnitude of Raman activity depends on the deviation of polarizability along the vibrational coordinate and the polarizability is the quantity to indicate how much (and which direction) the molecule can induce the dipole moment or deviate the charge distribution, or in fact deviate the electron distribution. It turns out that the Raman activity depends on how the size and shape of electron cloud would deviate as a whole along the vibrational coordinate. This condition is realized for the change in bond length and angle, and eventually Raman spectrum is sensitive to skeletal structure and its change along the vibrational mode. On the other hand, infrared activity depends on how charge distribution changes along the vibrational coordinate. Therefore, the infrared spectrum is sensitive to functional groups located at the edge of molecule and Raman spectrum is sensitive to the skeletal

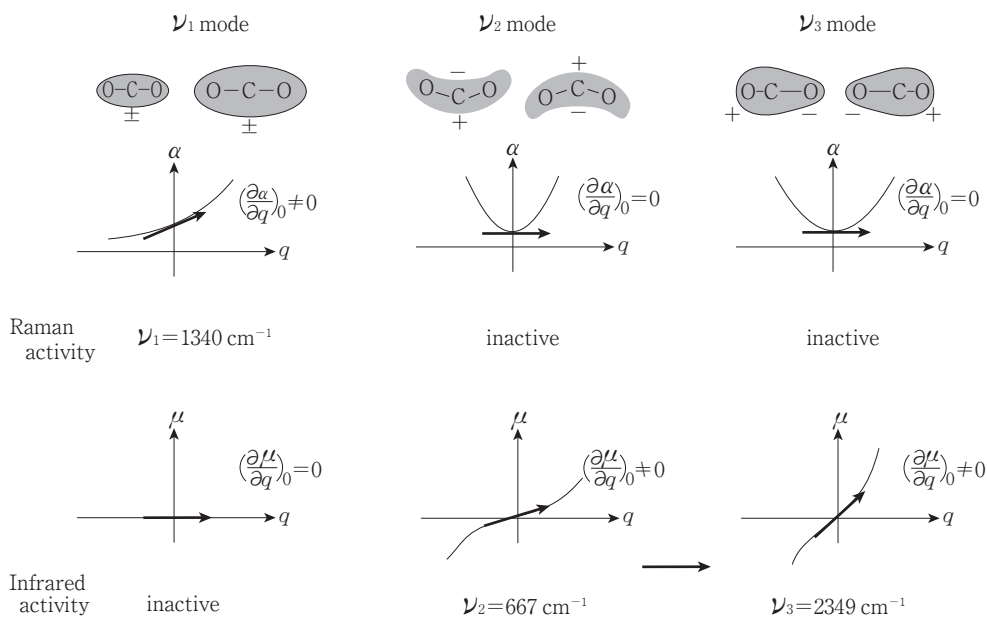


Fig.6 Raman and Infrared activities as exemplified by CO_2

The shadowed area denotes the electron cloud and its volume roughly denotes the magnitude of polarizability. The positions of the signs, + and -, show the centers of their charges qualitatively. The sign, \pm , denotes the coincidence of the two centers.

structure. These considerations are empirically verified.

Fig. 6 shows the pictorial idea of Raman activity and infrared activity. In case of CO_2 molecule, the band (ν_1 : symmetric stretching) which appears in Raman spectrum does not appear as infrared spectrum, while the infrared active bands (ν_3 : anti-symmetric stretching and ν_2 : bending) do not appear as Raman spectrum. This is known as mutual exclusion rule for the molecule that has a center of symmetry.

Now we consider the intensity of Raman spectrum. According to the classical electro-

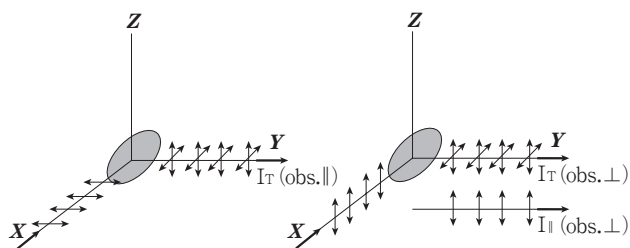


Fig.7 Relation between polarizations of incident and scattered lights

magnetism, the total radiation emitted per unit solid angle in one-direction by oscillating dipole moment is given by

$$I = \frac{2\pi^3\nu^4}{c^3}\boldsymbol{\mu}^2. \quad (2-7)$$

We are considering the case that the emitting dipole moment is induced by the electric field of incident light so that $\boldsymbol{\mu} = \alpha\mathbf{E}$ as given by 2-2). By substituting this relation into 2-7), we obtain

$$I = \frac{2\pi^3\nu^4}{c^3}\alpha^2\mathbf{E}^2. \quad (2-8)$$

The intensity of incident radiation I_i is connected with the amplitude of electric field vector \mathbf{E} as

$$I_i = \frac{c}{8\pi}\mathbf{E}^2. \quad (2-9)$$

Substituting this relation into 2-8), we obtain

$$I = \frac{16\pi^4\nu^4}{c^4}I_i\alpha^2. \quad (2-10)$$

The equation 2-10) tells that the Raman intensity is proportional to the 4th power of frequency. That means that higher frequency or short wavelength is effective to obtain stronger Raman signal. However, sometimes we have a disturbance of fluorescence when the exciting wavelength approaches to the electronic absorption region. This is one of the practical problems of experimental Raman spectroscopy. Of course, there are many strategies to overcome this problem. But descriptions of these methods are out of this article.

Since the polarizability α is a tensor quantity as described above, the vector of emitted light is not necessarily parallel to that of incident light. Let's take laboratory fixed space X , Y , and Z , and assume that the plane-polarized incident light comes into sample from X direction and scattered light is observed along Y direction as shown in Fig.7. We can classify the scattered lights as designated by the following equations according to the relation of directions of incident electric vector and observation,

$$I_T(\text{obs. } \parallel) = \frac{2\pi^3\nu^4}{c^3}(\alpha_{xy}^2 + \alpha_{zy}^2)\mathbf{E}^2, \quad (2-11)$$

$$I_T(\text{obs. } \perp) = \frac{2\pi^3\nu^4}{c^3}(\alpha_{xz}^2 + \alpha_{zz}^2)\mathbf{E}^2. \quad (2-12)$$

The polarized part parallel to E is especially expressed by

$$I_{\parallel}(\text{obs. } \perp) = \frac{2\pi^3\nu^4}{c^3}\alpha_{zz}^2\mathbf{E}^2. \quad (2-13)$$

Above three equations are applied for a single radiator which is fixed to the laboratory coordinate. If we want to obtain the expressions for a system where molecules are freely rotate in the space, we must deduce the averaged expression of polarizability elements $\alpha_{FF'}$ of laboratory-fixed coordinates from those, $\alpha_{gg'}$, of the molecule-fixed coordinates. The gener-

al formulas of transformation combining $\alpha_{FP'}$ and $\alpha_{gg'}$ is

$$\alpha_{FP'} = \sum_{gg'} \alpha_{gg'} \Phi_{F'g} \Phi_{Fg}. \quad (2-14)$$

where $\alpha_{F'g}$ is the direction cosines between laboratory-fixed coordinate F' and molecule-fixed coordinate g . We can always determine the principal axes of particular molecule, therefore 2-14) can be a little bit simplified to

$$\alpha_{FP'} = \sum_{i=1}^3 \alpha_i \Phi_{F'i} \Phi_{F'i}. \quad (2-15)$$

After some calculations, we can figure out the next equations,

$$I_{\parallel}(\text{obs.}) = \frac{1}{15} \frac{16\pi^4 \nu^4}{c^4} N I_0 (2 \sum_i \alpha_i^2 - 2 \sum_{i < j} \alpha_i \alpha_j), \quad (2-16)$$

$$I_{\perp}(\text{obs.}) = \frac{1}{15} \frac{16\pi^4 \nu^4}{c^4} N I_0 (4 \sum_i \alpha_i^2 + \sum_{i < j} \alpha_i \alpha_j), \quad (2-17)$$

$$I_1(\text{obs.}) = \frac{1}{15} \frac{16\pi^4 \nu^4}{c^4} N I_0 (3 \sum_i \alpha_i^2 + 2 \sum_{i < j} \alpha_i \alpha_j), \quad (2-18)$$

where N is the number of molecules and I_0 is the intensity of incident radiation. Summations appearing in the above three equations can be replaced by functions of the spherical part of the polarizability, α , and the anisotropy, β , which are defined by

$$\alpha = \frac{1}{3} (\alpha_1 + \alpha_2 + \alpha_3), \quad (2-19)$$

$$\beta = \frac{1}{2} [(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2]. \quad (2-20)$$

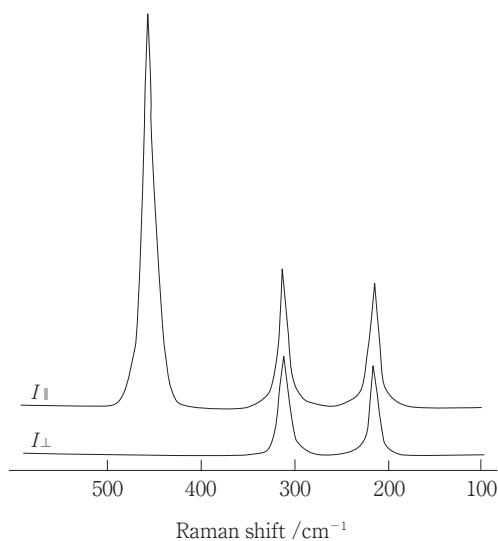


Fig.8 Raman spectrum of CCl_4 and depolarization ratio

Equations 2-16) to 2-18) are rewritten, in terms of the above quantities, by

$$I_{\text{T}}(\text{obs.}\parallel) = \frac{16\pi^4\nu^4}{c^4}NI_0\frac{2\beta^2}{15}, \quad 2-21)$$

$$I_{\text{T}}(\text{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4}NI_0\frac{45\alpha^2+7\beta^2}{45}, \quad 2-22)$$

$$I_{\text{I}}(\text{obs.}\perp) = \frac{16\pi^4\nu^4}{c^4}NI_0\frac{45\alpha^2+4\beta^2}{45}. \quad 2-23)$$

For the interpretation of vibrational modes, the depolarization ratio is often used, which is defined by

$$\rho_i = \frac{I_{\perp}}{I_{\parallel}}, \quad 2-24)$$

for a linear (plane) polarized incident light. Substituting 2-21~23) into 2-24), we obtain the following relation,

$$\rho_i = \frac{I_{\text{T}}(\text{obs.}\perp) - I_{\text{I}}(\text{obs.}\perp)}{I_{\text{I}}(\text{obs.}\perp)} = \frac{3\beta^2}{45\alpha^2+4\beta^2}. \quad 2-25)$$

If the polarization tensor is perfectly isotropic such as totally symmetric C-Cl stretching, the anisotropy term is zero ($\beta^2=0$). Therefore, we have $\rho_i=0$ as shown in Fig.8. On the other hand, the depolarization ratio of non-totally symmetric mode is 3/4 ($\rho_i=3/4$), where $\alpha_{\gamma\gamma}=0$, ($\gamma=x, y, z$) and $\alpha_{\gamma\gamma'}\neq 0$, ($\gamma\neq\gamma'$). In general, we have $0 < \rho_i < 3/4$ for totally symmetric modes with $\alpha_{\gamma\gamma}\neq 0$, and $\rho_i = 3/4$ for non-totally symmetric modes. The depolarization ratio is a useful piece of information to determine the symmetry of the vibrational mode.

We have now deduced some formulae necessary for analyzing Raman spectrum. However, for further detailed understanding of Raman process, we need to develop the physical background based on quantum physics. One of the final answer in this review is to obtain the quantum mechanical representation for Raman tensor, that is

$$(\alpha_{\sigma\rho})_{mn} = \sum \left[\frac{\langle n | \mu_{\rho} | e \rangle \langle e | \mu_{\sigma} | m \rangle}{\hbar(\nu_{em} - \nu_i) + i\Gamma_e} + \frac{\langle n | \mu_{\sigma} | e \rangle \langle e | \mu_{\rho} | m \rangle}{\hbar(\nu_{em} - \nu_i) + i\Gamma_e} \right], \quad 2-26)$$

where $\alpha_{\sigma\rho}$ is $\sigma\rho$ component of Raman scattering tensor, e containing every eigenstate in the electronic excited states, and ν_{em} is transition frequency from state m to e . $\langle n | \mu_{\rho} | e \rangle$, $\langle n | \mu_{\sigma} | m \rangle$, \dots are the components of transition electric dipole moments, and μ_{ρ} is the electric dipole moment operator in ρ direction. Γ_e is a damping factor of the e state. The equation 2-26) is the fundamental formula for Raman scattering, and is called Kramers-Heisenberg-Dirac dispersion equation.

III. Quantization of Electromagnetic Field

3-1. Electromagnetic field and charged particle

Spectroscopy deals with the absorption and emission of radiation by molecules, in other

words the interaction between photon and molecule. This process should be treated by quantum mechanics if we want to interpret the phenomenon quantitatively. Therefore, we need to derive the quantum mechanical description of the electromagnetic radiation. We will start to summarize the classical electromagnetism to the extent necessary to spectroscopy.

The electromagnetic phenomenon where exists charged particle and electric current is described by the following four Maxwell-Lorentz equations

$$\text{rot}\mathbf{H}=\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}+\frac{4\pi}{c}\mathbf{i}, \quad 3-1)$$

$$\text{rot}\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}, \quad 3-2)$$

$$\text{div}\mathbf{H}=0, \quad 3-3)$$

$$\text{div}\mathbf{E}=4\pi\rho, \quad 3-4)$$

where the physical quantities are defined as follow, c : velocity of light, \mathbf{H} : magnetic field, \mathbf{E} : electric field, \mathbf{i} : electric current density, ρ : charge density. If the charge is moving with a speed of \mathbf{V} , the following relation is approved,

$$\mathbf{i}=\rho\mathbf{V}. \quad 3-5)$$

Also the electric current density and charge density should satisfy the following relation,

$$\frac{\partial\rho}{\partial t}+\text{div}\mathbf{i}=0. \quad 3-6)$$

This relation is instantly derived from 3-1) by operating div both sides, knowing the vector operation rule, $\text{div}\text{rot}\mathbf{f}\equiv 0$. This equation is called as continuation equation. In general, a vector \mathbf{f} can be represented by rot of some other vector, if the \mathbf{f} satisfies the relation of $\text{div}\mathbf{f}=0$. Then, 3-3) is rewritten by

$$\mathbf{H}=\text{rot}\mathbf{A}. \quad 3-7)$$

Substituting this relation into 3-2), we obtain

$$\text{rot}\left(\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}\right)=0. \quad 3-8)$$

Also, in general, a vector \mathbf{d} can be represented by grad of some scalar quantity, if the \mathbf{d} satisfies the relation of $\text{rot}\mathbf{d}=0$. Therefore, 3-8) is rewritten by

$$\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}=-\text{grad}\phi. \quad 3-9)$$

The minus sign of right side of the equation is put at some convenience. The quantities, \mathbf{A} and ϕ , thus introduced and defined are called vector potential and scalar potential. Now, we introduce arbitrary function of position and time, λ . Let replace \mathbf{A} and ϕ by the following relations,

$$\mathbf{A}' = \mathbf{A} + \text{grad}\lambda, \quad \phi' = \phi - \frac{1}{c} \frac{\partial \lambda}{\partial t}. \quad (3-10)$$

This is called gauge transformation. Substituting 3-10) into 3-9), we obtain the next homological equation, like

$$\mathbf{H} = \text{rot}\mathbf{A}', \quad \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}'}{\partial t} = -\text{grad}\phi'. \quad (3-11)$$

This means that the above definition cannot determine \mathbf{A} and ϕ uniquely. Therefore, we can introduce the next additional condition that is called Lorentz condition,

$$\frac{1}{c} \frac{\partial \phi}{\partial t} + \text{div}\mathbf{A} = 0. \quad (3-12)$$

Substituting 3-7) and 3-9) into 3-1), and taking 3-12) and the next vector operations, $\text{rot rot} = \text{grad div} - \Delta$ and $\text{div grad} = \Delta$ (where Δ is Laplace operator), into consideration, we can derive next two equations,

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \Delta \mathbf{A} = \frac{4\pi}{c} \mathbf{i} \quad (3-13)$$

$$\frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} - \Delta \phi = 4\pi\rho. \quad (3-14)$$

These equations can be simplified to the next d'Alembert equation

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \Delta \right) \Phi = 0, \quad (3-15)$$

when $\mathbf{i} = \rho = 0$, where Φ is any one of ϕ , \mathbf{A} , \mathbf{E} , and \mathbf{H} . The expression of 3-15) is a typical formula of wave, that is, the electromagnetic field in vacuum behaves like a kind of wave.

An electron under electric and magnetic field is subjected to the Lorentz force which is represented by

$$\mathbf{f} = -e \left(\mathbf{E} + \frac{1}{c} [\mathbf{V}, \mathbf{H}] \right). \quad (3-16)$$

Therefore, the equation of motion of electron is described by

$$m_e \frac{d^2 \mathbf{r}}{dt^2} = \frac{e}{c} \left(\frac{\partial \mathbf{A}}{\partial t} + \left[\frac{d\mathbf{r}}{dt}, \text{rot} \mathbf{A} \right] + c \text{grad}\phi \right), \quad (3-17)$$

where \mathbf{r} is the position vector of electron. Here we introduce two functions defined by

$$H = \frac{1}{2m_e} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 - e\phi, \quad (3-18)$$

$$\mathbf{p} = m_e \frac{d\mathbf{r}}{dt} - \frac{e}{c} \mathbf{A}. \quad (3-19)$$

Here H is a function of independent variables of x , y , z , p_x , p_y , p_z , and t . Combining these two equations with 3-17), we can prove that next relations are satisfied,

$$-\frac{\partial H}{\partial \alpha} = \frac{dp_\alpha}{dt} \quad (\alpha = x, y, z) \quad \text{and} \quad -\frac{\partial H}{\partial p_\alpha} = \frac{d\alpha}{dt} \quad (\alpha = x, y, z). \quad (3-20)$$

In these derivations, we take the relation of $\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{\partial x}{\partial t} \frac{\partial}{\partial x} + \frac{\partial y}{\partial t} \frac{\partial}{\partial y} + \frac{\partial z}{\partial t} \frac{\partial}{\partial z}$ into consideration. The equation 3-20) shows that H is a Hamilton function of the system, and this is the Hamilton's canonical equation of motion, and \mathbf{p} is a momentum canonical conjugate to \mathbf{r} .

To convert the problem into that of quantum mechanics, we must obey the general rule that classical momentum should be replaced by its differential operator such that

$$p_\alpha \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \alpha}, (\alpha = x, y, z). \quad 3-21)$$

Then, the Schrödinger equation for one electron under electromagnetic field is given by

$$H = \Psi(x, y, z, t) = \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(x, y, z, t), \quad 3-22)$$

$$\begin{aligned} H &= \frac{1}{2m_e} \sum_{\alpha=x,y,z} \left(\frac{\hbar}{i} \frac{\partial}{\partial \alpha} + \frac{e}{c} \mathbf{A}_\alpha \right)^2 - e\phi + \mathbf{V} \\ &= -\frac{\hbar^2}{2m_e} \Delta - \frac{i\hbar e}{m_e c} (\mathbf{A} \cdot \text{grad}) - \frac{i\hbar e}{2m_e c} \text{div} \mathbf{A} + \frac{e^2}{2m_e c^2} \mathbf{A}^2 - e\phi + \mathbf{V}. \end{aligned} \quad 3-23)$$

The equation 3-23) can be rewritten for the general charged particles as follows

$$H = \sum_{p(\text{particles})} \frac{1}{2m_p} \left(\frac{\hbar}{i} (\text{grad})_p - \frac{e_p}{c} \mathbf{A}_p \right)^2 + e_p \phi_p + \mathbf{V}. \quad 3-24)$$

3-2. Induced polarization and optical rotation

We will consider electric and magnetic moments induced in atom or molecule under oscillating electromagnetic field. Let the system be in a stationary state represented by the following wave function,

$$\Psi_n^{(0)} = \psi_n^0 \exp(-i \frac{E_n}{\hbar} t). \quad 3-25)$$

The system of quantum number, n , at the beginning (that is $c_n(t) \approx 1$) is perturbed by the electromagnetic field and the wave function for the weak field is now described by the ordinary expansion as

$$\Psi = \Psi_n^{(0)} + \sum_{m \neq n} c_m(t) \psi_m^0 \exp(-i \frac{E_m}{\hbar} t). \quad 3-26)$$

Time evolution of coefficient $c_m(t)$ is written by

$$\frac{dc_m}{dt} = -\frac{i}{\hbar} \sum_{m \neq n} c_m(t) \langle \psi_m^0 | H' | \psi_n^0 \rangle \exp(-i \frac{E_m - E_n}{\hbar} t), \quad 3-27)$$

where H' is a perturbing Hamiltonian.

The perturbing Hamiltonian H' is a difference of 3-23) and that derived from 2-23) by putting $\mathbf{A} = \phi = 0$. Under this condition, we can derive the relation of $\text{div} \mathbf{A} = 0$ from Lorentz condition (3-12)). The effect of \mathbf{A}^2 can be ignored for electromagnetic field not extremely strong. Then H' is written by

$$H' = \sum_j \frac{i\hbar p_j}{m_j c} \mathbf{A}_j (\text{grad})_j. \quad (3-28)$$

The vector potential \mathbf{A}_j in the molecule can be expanded by

$$\mathbf{A}_j = \mathbf{A}_0 + \mathbf{r}_j (\text{grad} \mathbf{A}_0) + \dots, \quad (3-29)$$

where the origin of the coordinates is fixed in the molecule and indicated by suffix 0. Substituting this equation into 3-28) we obtain

$$H' = \sum_j \frac{i\hbar p_j}{m_j c} \left\{ \mathbf{A}_0 (\text{grad})_j + \frac{1}{2} (\text{rot} \mathbf{A})_0 \cdot [\mathbf{r}_j \times (\text{grad})_j] + [Q] + \dots \right\}, \quad (3-30)$$

where

$$\begin{aligned} [Q] &= \left\{ \left(\frac{\partial A_x}{\partial x} \right)_0 x_j \frac{\partial}{\partial x_j} + \left(\frac{\partial A_y}{\partial y} \right)_0 y_j \frac{\partial}{\partial y_j} + \left(\frac{\partial A_z}{\partial z} \right)_0 z_j \frac{\partial}{\partial z_j} \right\} \\ &= \frac{1}{2} \left\{ \left(\frac{\partial A_x}{\partial y} + \frac{\partial A_y}{\partial x} \right)_0 \left(y_j \frac{\partial}{\partial z_j} + z_j \frac{\partial}{\partial y_j} \right) + \left(\frac{\partial A_x}{\partial z} + \frac{\partial A_z}{\partial x} \right)_0 \left(z_j \frac{\partial}{\partial x_j} + x_j \frac{\partial}{\partial z_j} \right) \right. \\ &\quad \left. + \left(\frac{\partial A_y}{\partial x} + \frac{\partial A_x}{\partial y} \right)_0 \left(x_j \frac{\partial}{\partial y_j} + y_j \frac{\partial}{\partial x_j} \right) \right\}. \end{aligned} \quad (3-31)$$

We can now obtain the matrix elements for the interaction between radiation and particle system by substituting 3-30) into 3-27). The matrix element derived from the first term of 3-30) is

$$\langle \Psi_m^{(0)*} | \sum_j \frac{i\hbar p_j}{m_j c} \mathbf{A}_0 (\text{grad})_j | \Psi_n^{(0)} \rangle = -\frac{i}{\hbar c} (E_m - E_n) \mathbf{A}_0 \mu_{mn} \exp\left(i \frac{E_m - E_n}{\hbar} t\right). \quad (3-32)$$

Here μ_{mn} is given by

$$\mu_{mn} = \int \Psi_m^* \hat{\mu} \Psi_n d\tau. \quad (3-33)$$

and $\hat{\mu}$ is an electric dipole moment operator as defined by $\hat{\mu} = \sum_j p_j \mathbf{r}_j$.

Remembering that orbital angular momentum of particle j is represented by $\mathbf{m}_j = -i\hbar (\mathbf{r}_j \times (\text{grad})_j)$ and taking 3-7) into consideration, the second term of H' is written by

$$-\sum_j \frac{p_j}{2m_j c} \mathbf{H}_0 \mathbf{m}_j = -(\mathbf{m} \mathbf{H}_0) \left(\mathbf{m} = \sum_j \frac{p_j}{2m_j c} \mathbf{m}_j \right). \quad (3-34)$$

This is the term due to magnetic moment. Also it is verified that the third term in 3-30) represents electric quadrupole moment.

Thus higher order electric and magnetic moments give the matrix elements of H' . Substituting the calculated matrix element of H' into 3-27) and integrating the equation, we have time dependent coefficient c_m , and then substituting this value into 3-26), we can evaluate how the other states are mixed into the initial state. Therefore, the perturbed state gains the electric and magnetic moments due to the mixing of the other moments other than the initial moment. These are called the induced moments. They are given by

$$\text{Induced electric moment : } \boldsymbol{\mu}' = \alpha \mathbf{E}' + \gamma \mathbf{H}' - \frac{1}{c} \beta \frac{d\mathbf{H}'}{dt}. \quad 3-35)$$

$$\text{Induced magnetic moment : } \mathbf{m}' = \kappa \mathbf{H}' + \gamma \mathbf{E}' + \frac{1}{c} \beta \frac{d\mathbf{E}'}{dt}. \quad 3-36)$$

Here E' and H' are the effective radiation field in the molecule. The coefficients in 3-35) and 3-36) are given by

$$\alpha = \frac{2}{3h} \sum_m \nu_{mn} \frac{|\langle n | \boldsymbol{\mu} | m \rangle|^2}{\nu_{mn}^2 - \nu^2}, \quad 3-37)$$

$$\kappa = \frac{2}{3h} \sum_m \nu_{mn} \frac{|\langle n | \mathbf{m} | m \rangle|^2}{\nu_{mn}^2 - \nu^2}, \quad 3-38)$$

$$\gamma = \frac{2}{3h} \sum_m \nu_{mn} \frac{\text{Re} \{ \langle n | \boldsymbol{\mu} | m \rangle \langle m | \mathbf{m} | n \rangle \}}{\nu_{mn}^2 - \nu^2}, \quad 3-39)$$

$$\beta = \frac{c}{3\pi h} \sum_m \frac{\text{Im} \{ \langle n | \boldsymbol{\mu} | m \rangle \langle m | \mathbf{m} | n \rangle \}}{\nu_{mn}^2 - \nu^2}. \quad 3-40)$$

Here ν is the frequency of radiation and $\nu_{mn} = (E_m - E_n)/h$. The magnitude of the matrix elements of $\boldsymbol{\mu}$ is bigger than those of \mathbf{m} , and α is far greater than the other three values in 3-38) to 3-40). α is called polarizability and κ is called magnetic susceptibility. β is related to optical rotatory or optical activity.

IV. Harmonic Oscillator and Ladder Operators

As the preparation for the following discussions, we will summarize the fundamental properties of the harmonic oscillator. The Hamiltonian of one dimensional oscillator of mass m and frequency ω is described by

$$H = \frac{p^2}{2m} + \frac{m}{2} \omega^2 q^2. \quad 4-1)$$

To convert this equation to that in quantum mechanics, the angular momentum should be replaced by derivative operator as described in 3-21). Then we have the Schrödinger equation corresponding to 4-1) as

$$\frac{\hbar^2}{2m} \left(-\frac{d^2}{dq^2} + \frac{1}{2} m \omega^2 q^2 \right) \psi(q) = E \psi(q), \quad 4-2)$$

and the eigenfunctions of the above equation are described by

$$\psi_n(q) = \frac{1}{2^{n/2} \sqrt{n!}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} q^2\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}} q\right), \quad 4-3)$$

where $H_n(x)$ is a Hermite polynomial of degree n and the eigenvalues are given by

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega. \quad 4-4)$$

If we change the variables as follows

$$\xi = \sqrt{\frac{m\omega}{\hbar}} q, \quad u_n = \sqrt{\frac{\hbar}{m\omega}} \psi_n, \quad 4-5)$$

the equation 4-3) can be written simply by

$$u_n(\xi) = \frac{1}{(\sqrt{\pi} 2^n n!)^{1/2}} \exp(-\xi^2/2) H_n(\xi). \quad 4-6)$$

New variable and function have the following properties.

$$\int_{-\infty}^{+\infty} u_n u_m d\xi = \delta_{nm}, \quad 4-7)$$

$$\frac{1}{\sqrt{2}} \left(\xi + \frac{d}{d\xi} \right) u_n = \sqrt{n} u_{n-1}, \quad 4-8)$$

$$\frac{1}{\sqrt{2}} \left(\xi - \frac{d}{d\xi} \right) u_n = \sqrt{n+1} u_{n+1}, \quad 4-9)$$

$$\xi u_n = \sqrt{\frac{n+1}{2}} u_{n+1} + \sqrt{\frac{n}{2}} u_{n-1}, \quad 4-10)$$

$$u_n(-\xi) = (-1)^n u_n(\xi). \quad 4-11)$$

We will investigate the characteristics of the harmonic oscillator, since it has a great expansible nature in quantum mechanics. Let us introduce new variables defined by

$$P^2 = p^2/m, \quad Q^2 = mq^2. \quad 4-12)$$

Then 4-1) is rewritten as

$$H = \frac{1}{2} (P^2 + \omega^2 Q^2). \quad 4-13)$$

The transition to quantum mechanics is accomplished by reinterpreting P and Q as Hermitian operator which obey the following commutation relation

$$[Q, P] = i\hbar. \quad 4-14)$$

This is equivalent to the replacement of P by $-i\hbar \partial / \partial Q$. Now, let us define the two operators by the linear combination of Q and P as

$$a = \frac{1}{\sqrt{2\hbar\omega}} (\omega Q + iP), \quad a^\dagger = \frac{1}{\sqrt{2\hbar\omega}} (\omega Q - iP), \quad 4-15)$$

or

$$Q = \sqrt{\frac{\hbar}{2\omega}} (a + a^\dagger), \quad P = i\sqrt{\frac{\hbar\omega}{2}} (a^\dagger - a). \quad 4-16)$$

It is easily shown that new operators have the following commutation relation

$$[a, a^\dagger] = 1, \quad 4-17)$$

which is equivalent to 4-14). And the Hamiltonian 4-13) is represented by

$$H = \frac{1}{2} \hbar\omega (a^\dagger a + a a^\dagger) = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) = \hbar\omega \left(N + \frac{1}{2} \right), \quad 4-18)$$

where

$$N = a^\dagger a \quad 4-19)$$

is called the number operator. Attention must be paid that N is Hermitian, although a and a^\dagger are not Hermitian. Knowing the commutation relation of 4-17), the next relations are also approved,

$$Na = a^\dagger aa = (aa^\dagger - 1)a = a(a^\dagger a - 1) = a(N - 1), \quad 4-20)$$

$$Na^\dagger = a^\dagger aa^\dagger = a^\dagger(aa^\dagger + 1) = a^\dagger(N + 1). \quad 4-21)$$

Let $|n\rangle$ be an eigenstate of N with eigenvalue n , that is

$$N|n\rangle = n|n\rangle. \quad 4-22)$$

Since N is Hermitian, the eigenvalue n is real and the next relation is required, that is

$$\langle n' | n \rangle = \delta_{n'n}. \quad 4-23)$$

From 4-20) and 4-22),

$$Na|n\rangle = a(N-1)|n\rangle = aN|n\rangle - a|n\rangle = an|n\rangle - a|n\rangle = (n-1)a|n\rangle, \quad 4-24)$$

and from 4-21) and 4-22),

$$Na^\dagger|n\rangle = a^\dagger(N+1)|n\rangle = a^\dagger N|n\rangle + a^\dagger|n\rangle = a^\dagger n|n\rangle + a^\dagger|n\rangle = (n+1)a^\dagger|n\rangle. \quad 4-25)$$

Thus we have the result that if $|n\rangle$ is an eigenstate of N with eigenvalue n , then $a|n\rangle$ is also an eigenstate of N with eigenvalue $n-1$.

After some algebra and taking the boundary condition, we can reach the following equations

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad 4-26)$$

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad 4-27)$$

Thus the operators a and a^\dagger have been given the names annihilation and creation operators, respectively. They have the effects that step down and up the operated eigenstate.

V. Quantum Theory of Raman Activity

5-1. Hamiltonian of the Radiation Field

The electromagnetic field in vacuum can be represented by the following Maxwell equation in MKS unit, and by using only \mathbf{E} and \mathbf{B} ,

$$\text{rot } \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \quad 5-1)$$

$$\text{rot } \mathbf{B} - \epsilon_0 \mu_0 \frac{\partial \mathbf{E}}{\partial t} = 0, \quad 5-2)$$

$$\text{div } \mathbf{B} = \text{div } \mathbf{E} = 0, \quad 5-3)$$

where the relations of $\mathbf{D} = \epsilon_0 \mathbf{E}$ and $\mathbf{B} = \mu_0 \mathbf{H}$ are taking into account.

Furthermore, $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ are not independent and they are completely represented by a single vector potential $\mathbf{A}(\mathbf{r}, t)$, which defined by

$$\mathbf{B} = \text{rot } \mathbf{A}. \quad 5-4)$$

The relations in eq. 4-3) are automatically satisfied by vector identity relations.

Substituting 5-4) into 5-1), we obtain the following equation

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}. \quad 5-5)$$

Then substituting 5-4) and 5-5) into 5-2), the differential equation for \mathbf{A} to be determined is derived as

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0, \quad 5-6)$$

where

$$c = \sqrt{\frac{1}{\epsilon_0 \mu_0}} \quad 5-7)$$

is the speed of electromagnetic field in vacuum. For the relation $\text{div} \mathbf{E} = 0$ in 5-3) to be fulfilled, the next relation must be satisfied, that is

$$\text{div} \mathbf{A} = 0. \quad 5-8)$$

This is also verified in the preceding chapter.

Let $\mathbf{A}(\mathbf{r}, t)$ be represented by a Fourier expansion of oscillators as

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)) = 0, \quad 5-9)$$

where \mathbf{k} is a propagation vector. By substituting 5-9) into 5-6), we can obtain the relation

$$(k_x^2 + k_y^2 + k_z^2) = \frac{1}{c^2} \omega^2, \quad 5-10)$$

and knowing $|\mathbf{k}| = k$, we have

$$\omega = ck. \quad 5-11)$$

Substituting 5-9) into 5-8), we have the following relation,

$$\text{div} \mathbf{A} = i(\mathbf{A}_0 \cdot \mathbf{k}) \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)) = 0. \quad 5-12)$$

For the above equation to be satisfied, the next relation has to be approved

$$\mathbf{A}_0 \cdot \mathbf{k} = 0. \quad 5-13)$$

That is, \mathbf{A}_0 is perpendicular to the \mathbf{k} vector. This shows the radiation field \mathbf{A} is transversal wave. Let introduce a unit vector \mathbf{e} which lies in the direction of \mathbf{A} , that is

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \mathbf{e} \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)). \quad 5-14)$$

Substituting this relation into 5-4) and 5-5), the following relations are deduced

$$\mathbf{E}(\mathbf{r}, t) = i\omega \mathbf{A}_0 \mathbf{e} \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)), \quad 5-15)$$

$$\mathbf{B}(\mathbf{r}, t) = i[\mathbf{k} \times \mathbf{e}] \mathbf{A}_0 \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)). \quad 5-16)$$

For \mathbf{E} and \mathbf{B} to have physical meaning as natural phenomenon, these vectors should be real. Therefore, 5-14) can be rewritten by the following equations,

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{e} \{ \mathbf{A}_k(t) e^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{A}_k^*(t) e^{-i\mathbf{k} \cdot \mathbf{r}} \}, \quad 5-17)$$

and

$$\mathbf{A}_k(t) = |\mathbf{A}_k| e^{-i(\omega t + \delta)}. \quad 5-18)$$

So far we assumed the radiation is to be linear polarized wave, that is the oscillation is in one spatial direction perpendicular to the propagation. General wave can oscillate in any

direction in plane perpendicular to the \mathbf{k} vector. This is expressed by using two unit vectors perpendicular to each other and also perpendicular to the \mathbf{k} vector. Therefore, the general formula for \mathbf{A} is

$$\mathbf{A}(\mathbf{r} \cdot t) = \sum_{\mathbf{k}} \sum_{\gamma=1}^2 \mathbf{e}_{k\gamma} \{ \mathbf{A}_{k\gamma}(t) \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{A}_{k\gamma}^*(t) \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} \}. \quad (5-19)$$

We may, if we so desire, replace the linear polarization vectors \mathbf{e}_{k1} and \mathbf{e}_{k2} by unit vectors which indicate circular polarization. This is accomplished by defining

$$\mathbf{e}_{k+1} = -\frac{1}{\sqrt{2}}(\mathbf{e}_{k1} + i\mathbf{e}_{k2}), \quad \mathbf{e}_{k-1} = -\frac{1}{\sqrt{2}}(\mathbf{e}_{k1} - i\mathbf{e}_{k2}). \quad (5-20)$$

These vectors satisfy the following equation,

$$\mathbf{e}_{k\gamma}^* \times \mathbf{e}_{k\gamma'} = i\gamma \mathbf{k} \delta_{\gamma\gamma'} \quad (\gamma, \gamma' = \pm 1). \quad (5-21)$$

With $\gamma = +1$ the cross product gives a vector parallel to the direction of propagation whereas $\gamma = -1$ the cross product is antiparallel. For this reason one refers to \mathbf{e}_{k+1} and \mathbf{e}_{k-1} as positive and negative helicity vectors. Also they represent left and right circular polarization according to standard optical convention.

According to the electromagnetism, the energy density of electromagnetic field is

$$W = \frac{1}{2}(\mathbf{D} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{H}) = \frac{1}{2}(\epsilon \mathbf{E}^2 + \frac{1}{\mu} \mathbf{B}^2). \quad (5-22)$$

Substituting 5-15) and 5-16) into 5-22) and generalizing them according to the procedure of 5-19), we obtain

$$W = \sum_{k,\gamma} (\omega_k^2 + c^2 k^2) (A_{k\gamma} A_{k\gamma}^* + A_{k\gamma}^* A_{k\gamma}) = \sum_{k,\gamma} 2\epsilon \omega_k^2 A_{k\gamma}^* A_{k\gamma}. \quad (5-23)$$

We now introduce a new set of variables

$$A_{k\gamma} = \frac{1}{2\sqrt{\epsilon \omega_k}} (\omega_k Q_{k\gamma} + iP_{k\gamma}), \quad A_{k\gamma}^* = \frac{1}{2\sqrt{\epsilon \omega_k}} (\omega_k Q_{k\gamma} - iP_{k\gamma}), \quad (5-24)$$

which, when substituted into 5-23), gives

$$W = \frac{1}{2} \sum_{k,\gamma} (P_{k\gamma}^2 + \omega_k^2 Q_{k\gamma}^2). \quad (5-25)$$

It is now shown that $P_{k\gamma}$ and $Q_{k\gamma}$ satisfy the Hamilton equations; this will identify these quantities as canonical variables and therefore W in the form 5-25) will be interpretable as the Hamiltonian of the electromagnetic field. Upon inverting 5-24),

$$Q_{k\gamma} = \frac{1}{2}(A_{k\gamma} + A_{k\gamma}^*), \quad P_{k\gamma} = -i\frac{1}{2}(A_{k\gamma} - A_{k\gamma}^*). \quad (5-26)$$

5-2. Quantization of the Radiation Field

Having identified the Hamiltonian of each mode of an electromagnetic field with that of a harmonic oscillator we may proceed the quantization exactly as in the case of the harmonic oscillator described in chapter 4. The transition to quantum mechanics is accom-

plished by interpreting $P_{k\gamma}$ and $Q_{k\gamma}$ as operators that satisfy the commutation relations

$$[Q_{k\gamma}, P_{k'\gamma'}] = i\hbar \delta_{kk'} \delta_{\gamma\gamma'}, \quad [Q_{k\gamma}, Q_{k'\gamma'}] = [P_{k\gamma}, P_{k'\gamma'}] = 0. \quad (5-27)$$

By analogy with 4-15), we define

$$a_{k\gamma} = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k Q_{k\gamma} + iP_{k\gamma}), \quad a_{k\gamma}^\dagger = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k Q_{k\gamma} - iP_{k\gamma}). \quad (5-28)$$

In terms of these operators the Hamiltonian denoted by 5-25) becomes

$$H = \sum_{k\gamma} \hbar\omega_k (a_{k\gamma}^\dagger a_{k\gamma} + \frac{1}{2}) = \sum_{k\gamma} \hbar\omega_k (N_{k\gamma} + \frac{1}{2}), \quad (5-29)$$

in which $N_{k\gamma}$ is known as the number operator for mode \mathbf{k} and polarization λ and is given by

$$N_{k\gamma} = a_{k\gamma}^\dagger a_{k\gamma}. \quad (5-30)$$

We can easily deduce the energies of the radiation system as

$$E = \sum_{k\gamma} E_{k\gamma} = \sum_{k\gamma} \hbar\omega_k (n_{k\gamma} + \frac{1}{2}). \quad (5-31)$$

5—3. Interaction Hamiltonian and Matrix Elements

The general form of 3-18) for one electron system is

$$H = \frac{1}{2m} (\mathbf{p} - e\mathbf{A})^2. \quad (5-32)$$

Here m is the mass of electron and \mathbf{p} is the momentum of electron and \mathbf{A} is the vector potential. The extension to the general molecular system should be straightforward now.

The total Hamiltonian for a radiation field and a molecular system may be written as

$$H = H_{\text{rad}} + H_{\text{molecule}} + H_{\text{int}}. \quad (5-33)$$

Here

$$\begin{aligned} H_{\text{rad}} &= \sum_{k\lambda} \hbar\omega_k (a_{k\lambda}^\dagger a_{k\lambda} + \frac{1}{2}), \\ H_{\text{molecule}} &= \sum_{i,a} (p_{i,a}^2/m_i) + V. \end{aligned} \quad (5-34)$$

The interaction between radiation field and molecule comes from the terms which have the vector potential \mathbf{A} in 5-32). That is

$$H_{\text{int}} = -\frac{e}{m} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2m} \mathbf{A}^2. \quad (5-35)$$

The first term of the above equation is rewritten as

$$H_1 = \sum_{k\lambda} (e/m) \sqrt{2\pi\hbar/\omega_k V} (\mathbf{e}_{k\lambda} \cdot \mathbf{p}) [a_{k\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + a_{k\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}], \quad (5-36)$$

where V is the volume of the cavity for the radiation field. We will replace the coefficient before the vector representation to K in the following discussions. Then 5-36) is split into two terms

$$H_1^{(-)} = \sum_{k\lambda} K(\mathbf{e}_{k\lambda} \cdot \mathbf{p}) a_{k\lambda} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (5-37)$$

$$H_1^{(+)} = \sum_{k\lambda} K(\mathbf{e}_{k\lambda} \cdot \mathbf{p}) a_{k\lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (5-38)$$

The wave function of the interacting system will be a product of a molecular wave function, $|a\rangle$, and a wave function, $|n_1, n_2, \dots, n_i, \dots\rangle$, describing the radiation field, so that

$$|a; n_1, n_2, \dots, n_i, \dots\rangle. \quad (5-39)$$

Then the matrix element of $H_1^{(+)}$ in 5-38), for example, will be

$$\langle b; n_{k\lambda}+1 | H_1^{(+)} | a; n_{k\lambda} \rangle = K \sqrt{n_{k\lambda}+1} \langle b | (\mathbf{e}_{k\lambda} \cdot \mathbf{p}) e^{-i\mathbf{k} \cdot \mathbf{r}} | a \rangle, \quad (5-40)$$

where we used a matrix element derived from 4-28).

Matrix element of the type

$$\langle b | (\mathbf{e}_{k\lambda} \cdot \mathbf{p}) e^{-i\mathbf{k} \cdot \mathbf{r}} | a \rangle = \mathbf{e}_{k\lambda} \cdot \langle b | \mathbf{p} e^{-i\mathbf{k} \cdot \mathbf{r}} | a \rangle \quad (5-40')$$

may be simplified if $\mathbf{k} \cdot \mathbf{r} \ll 1$ so that,

$$\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} \approx 1. \quad (5-41)$$

Using the commutation rule, $[r_i, p^2] = 2i\hbar p_i$, we can derive the following commutation rule

$$[\mathbf{r}, H_{\text{molecule}}] = (i\hbar/m)\mathbf{p}. \quad (5-42)$$

Therefore

$$\begin{aligned} \langle b | \mathbf{p} | a \rangle &= (m/i\hbar) \langle b | [\mathbf{r}, H_{\text{molecule}}] | a \rangle \\ &= (i\hbar/m) (E_b - E_a) \langle b | \mathbf{r} | a \rangle = im\omega_k \langle b | \mathbf{r} | a \rangle. \end{aligned} \quad (5-43)$$

At the end, we have the matrix elements for $H_1^{(-)}$ and $H_1^{(+)}$ as

$$\langle b; n_{k\lambda}-1 | H_1^{(-)} | a; n_{k\lambda} \rangle = ieK \sqrt{n_{k\lambda}} \mathbf{e}_{k\lambda} \cdot \langle b | \mathbf{r} | a \rangle, \quad (5-44)$$

$$\langle b; n_{k\lambda}+1 | H_1^{(+)} | a; n_{k\lambda} \rangle = ieK \sqrt{n_{k\lambda}+1} \mathbf{e}_{k\lambda} \cdot \langle b | \mathbf{r} | a \rangle. \quad (5-45)$$

Equations 5-44) and 5-45) obviously shows the terms correlated with electric dipole transition. The next higher approximation for $e^{i\mathbf{k} \cdot \mathbf{r}}$ is

$$\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} \approx 1 + i\mathbf{k} \cdot \mathbf{r}, \quad (5-46)$$

and this higher term gives rise to the matrix elements related to magnetic dipole transition and electric quadrupole transition, but we skip the detail derivation which is out of scope of this article.

Now we will return to the Hamiltonian of 5-35). The representations by vector potential for 5-36) are shown in 5-37) and 5-38). That for second term of right hand side is written as

$$H_2 = K \sum_{k\lambda} \sum_{k'\lambda'} \frac{1}{\sqrt{\omega_k \omega_{k'}}} (\mathbf{e}_{k\lambda} \cdot \mathbf{e}_{k'\lambda'}) \times (a_{k\lambda} e^{i\mathbf{k} \cdot \mathbf{r}} + a_{k\lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}) (a_{k'\lambda'} e^{i\mathbf{k}' \cdot \mathbf{r}} + a_{k'\lambda'}^\dagger e^{-i\mathbf{k}' \cdot \mathbf{r}}). \quad (5-47a)$$

The quantities in the summation of the above equation can be rearranged to be

$$\frac{1}{\sqrt{\omega_k \omega_{k'}}} (\mathbf{e}_{k\lambda} \cdot \mathbf{e}_{k'\lambda'}) \left\{ \begin{aligned} & a_{k\lambda}^\dagger a_{k'\lambda'}^\dagger \exp[-i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] + a_{k\lambda} a_{k'\lambda'} \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] \\ & + a_{k\lambda} a_{k'\lambda'} \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] + a_{k\lambda} a_{k'\lambda'}^\dagger \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] \end{aligned} \right\}. \quad 5-47b)$$

In conclusion, the Hamiltonian H_2 is constituted of four parts,

$$H_2 = H_{k\lambda}^{(+)} H_{k'\lambda'}^{(+)} + H_{k\lambda}^{(-)} H_{k'\lambda'}^{(-)} + H_{k\lambda}^{(+)} H_{k'\lambda'}^{(-)} + H_{k\lambda}^{(-)} H_{k'\lambda'}^{(+)}, \quad 5-47c)$$

in which $H_{k\lambda}^{(+)} H_{k'\lambda'}^{(+)}$ refers to the term containing $a_{k\lambda}^\dagger a_{k'\lambda'}^\dagger$; $H_{k\lambda}^{(-)} H_{k'\lambda'}^{(-)}$ to the term with $a_{k\lambda} a_{k'\lambda'}$, and so on. Matrix elements of $a_{k\lambda}$ and $a_{k\lambda}^\dagger$ may be obtained as follows

$$\langle n_{k\lambda} + 1 | a_{k\lambda}^\dagger | n_{k\lambda} \rangle = \sqrt{n_{k\lambda} + 1}, \quad \langle n_{k\lambda} - 1 | a_{k\lambda} | n_{k\lambda} \rangle = \sqrt{n_{k\lambda}}. \quad 5-48)$$

The matrix elements of bilinear combinations of $a_{k\lambda}$ and $a_{k\lambda}^\dagger$ can be obtained from the above relations, and the change in the number of photons must be zero or two.

Raman scattering is a two-photon process from the initial state $|i\rangle$ to the final state $|f\rangle$ via the intermediate state $|l\rangle$. The matrix element of this process is represented by the second-order contribution of H_1 and the first-order contribution due to H_2 . The result of some derivations, we have

$$\begin{aligned} \langle f | H_{\text{int}} | i \rangle &= K \sqrt{\frac{n_{k\lambda} (n_{k'\lambda'} + 1)}{\omega_k \omega_{k'}}} (\mathbf{e}_{k\lambda} \cdot \mathbf{e}_{k'\lambda'}) \delta_{fi} \\ &\frac{1}{m} \sum_{\tau} \left[\frac{\langle f | \mathbf{e}_{k'\lambda'} \cdot \mathbf{p} | l \rangle \langle l | \mathbf{e}_{k\lambda} \cdot \mathbf{p} | i \rangle}{E_i - E_l + \hbar \omega_k} + \frac{\langle f | \mathbf{e}_{k\lambda} \cdot \mathbf{p} | l \rangle \langle l | \mathbf{e}_{k'\lambda'} \cdot \mathbf{p} | i \rangle}{E_i - E_l - \hbar \omega_{k'}} \right], \end{aligned} \quad 5-49)$$

where the dipole approximation is introduced whereby all exponentials are set equal to unity. Using this matrix element, we can derive the transition probability per unit time that an incident $\mathbf{k}\lambda$ photon has been scattered into the element of solid angle $d\Omega$ as a $\mathbf{k}'\lambda'$ photon, which is

$$\begin{aligned} W &= \left(\frac{e^2}{mc^2} \right) \frac{c}{V} \frac{\omega_k}{\omega_{k'}} d\Omega n_{k\lambda} (n_{k'\lambda'} + 1) \\ &\times \left| (\mathbf{e}_{k\lambda} \cdot \mathbf{e}_{k'\lambda'}) \delta_{fi} + \frac{1}{m} \sum_{\tau} \left[\frac{\langle f | \mathbf{e}_{k'\lambda'} \cdot \mathbf{p} | l \rangle \langle l | \mathbf{e}_{k\lambda} \cdot \mathbf{p} | i \rangle}{E_i - E_l + \hbar \omega_k} + \frac{\langle f | \mathbf{e}_{k\lambda} \cdot \mathbf{p} | l \rangle \langle l | \mathbf{e}_{k'\lambda'} \cdot \mathbf{p} | i \rangle}{E_i - E_l - \hbar \omega_{k'}} \right] \right|^2. \end{aligned} \quad 5-50)$$

The above equation is known as the Kramers-Heisenberg dispersion formula. This formula is also expressed as a differential scattering cross section, as

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{W}{d\Omega} \\ &= r_0^2 \frac{\omega_k}{\omega_{k'}} (n_{k'\lambda'} + 1) \times \left| (\mathbf{e}_{k\lambda} \cdot \mathbf{e}_{k'\lambda'}) \delta_{fi} + \frac{1}{m} \sum_{\tau} \left[\frac{(\mathbf{e}_{k'\lambda'} \cdot \mathbf{p}_{li})(\mathbf{e}_{k\lambda} \cdot \mathbf{p}_{if})}{E_i - E_l + \hbar \omega_k} + \frac{(\mathbf{e}_{k\lambda} \cdot \mathbf{p}_{li})(\mathbf{e}_{k'\lambda'} \cdot \mathbf{p}_{if})}{E_i - E_l - \hbar \omega_{k'}} \right] \right|^2, \end{aligned} \quad 5-51)$$

where $d\sigma$ is (number of $\mathbf{k}'\lambda'$ photons scattered / sec sr), $d\Omega$ is (number of incident $\mathbf{k}\lambda$ photons / sec cm^2), $r_0^2 = e^2/mc^2 =$ classical radius of the electron, and $\mathbf{p}_{if} = \langle f | \mathbf{p} | i \rangle$, $\mathbf{p}_{li} = \langle l | \mathbf{p} | i \rangle$.

To calculate the necessary terms in 5-51), we need to prepare some commutation relations for the operators that appear in the formula. The examples are the following types,

$$\langle f | \mathbf{e} \cdot \mathbf{p} | l \rangle = \frac{i\hbar}{\hbar} (E_f - E_l) \langle f | \mathbf{e} \cdot \mathbf{r} | l \rangle, \quad 5-52)$$

$$\mathbf{e}' \cdot \mathbf{e} \delta_{\beta} = \frac{m^2}{\hbar^2} \left[\frac{(E_l - E_i + \hbar\omega') \langle f | \mathbf{e}' \cdot \mathbf{r} | l \rangle \langle l | \mathbf{e} \cdot \mathbf{r} | i \rangle}{-(E_j - E_l + \hbar\omega') \langle f | \mathbf{e} \cdot \mathbf{r} | l \rangle \langle l | \mathbf{e}' \cdot \mathbf{r} | i \rangle} \right], \quad 5-53$$

where the notation so far used is simplified as follows

$$\mathbf{e}_{k\lambda} = \mathbf{e}, \mathbf{e}_{k'\lambda'} = \mathbf{e}', n_{k\lambda} = n, n_{k'\lambda'} = n', \omega_k = \omega, \omega_{k'} = \omega'. \quad 5-54$$

By replacing the above two type relations and knowing $E_j - E_i = \hbar\omega - \hbar\omega'$, we finally obtain

$$\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 (n' + 1) m^2 \times \left| \sum_l \left[\frac{\langle f | \mathbf{e}' \cdot \mathbf{r} | l \rangle \langle l | \mathbf{e} \cdot \mathbf{r} | i \rangle}{E_i - E_l + \hbar\omega} + \frac{\langle f | \mathbf{e} \cdot \mathbf{r} | l \rangle \langle l | \mathbf{e}' \cdot \mathbf{r} | i \rangle}{E_i - E_l - \hbar\omega} \right] \right|^2. \quad 5-55$$

This is the general form for Raman scattering as shown in 2-26).

VI. Raman Optical Activity

The interaction of a molecule with a dynamic electromagnetic field is needed to investigate the Raman optical activity (ROA) phenomenon. Assume that the time dependent, perturbed wave function, $\Psi_k(t)$, can be expressed by the unperturbed wave function $\Psi_n^0(t)$ using the time dependent coefficients $c_n(t)$ as

$$\Psi_k(t) = \sum_n c_n(t) \Psi_n^0(t). \quad 6-1$$

The time dependent coefficients $c_n(t)$ can be written as

$$c_n(t) = -\frac{i}{\hbar} \int \langle \Psi_n^0 | H_1(t) | \Psi_s^0 \rangle e^{i\omega_{ns}t} dt, \quad 6-2$$

where $\omega_{ns} = \frac{1}{\hbar} (E_n^0 - E_s^0)$. The above equation can be obtained by integrating 3-27) from time zero to a certain time.

Let us consider the influence of the dynamic field perturbation, which is weak, on the system. The time dependent electric dipole moment is given as

$$\mu_\alpha(t) = \langle \Psi_s(t) | \mu_\alpha | \Psi_s(t) \rangle, \quad 6-3$$

where α is the cartesian component, x, y or z . In case of the electric field perturbation, the first order correction of the Hamiltonian, $H_1(t)$, is expressed as

$$H_1(t) = -\mu_{\alpha'} E_{\alpha'}(t), \quad 6-4$$

where $\mathbf{E}(t)$ is the time dependent electric field. Notice that α' is representing the component of the field and is distinguished from the component of the electric dipole moment, α . Substituting 6-4) into 6-2), the coefficient is written as

$$c_n(t) = -\frac{i}{\hbar} \mu_{\alpha', ns} \int E_{\alpha'}(t) e^{i\omega_{ns}t} dt, \quad 6-5$$

where $\mu_{\alpha', ns} = \langle \Psi_n^0 | \mu_{\alpha'} | \Psi_s^0 \rangle$. When the applied electric field oscillates at ω frequency and is given as

$$E_{\alpha'}(t) = E_{\alpha'} [e^{i\omega t} + e^{-i\omega t}] = 2E_{\alpha'} \cos \omega t, \quad 6-6$$

the time dependent coefficient becomes

$$c_n(t) = 2\mu_{\alpha',ns} E_{\alpha'} e^{i\omega_{ns}t} \frac{(\omega_{ns} \cos \omega t - i\omega \sin \omega t - \omega_{ns} e^{-i\omega_{ns}t})}{\hbar(\omega_{ns}^2 - \omega^2)}. \quad (6-7)$$

From 6-1) and 6-3), $\mu_{\alpha}(t)$ can be obtained as

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) + 2\alpha_{\alpha\alpha'} E_{\alpha'} \cos \omega t - 2\alpha'_{\alpha\alpha'} E_{\alpha'} \sin \omega t + \dots \quad (6-8)$$

In this equation, $\alpha_{\alpha\alpha'}$ and $\alpha'_{\alpha\alpha'}$ are the frequency dependent electric dipole-electric dipole polarizabilities, and they are expressed as

$$\alpha_{\alpha\alpha'} = \text{Re} \left[\sum_{n \neq s} \frac{2\mu_{\alpha,sn} \mu_{\alpha',ns} \omega_{ns}}{\hbar(\omega_{ns}^2 - \omega^2)} \right], \quad (6-9)$$

$$\alpha'_{\alpha\alpha'} = \text{Im} \left[-\sum_{n \neq s} \frac{2\mu_{\alpha,sn} \mu_{\alpha',ns} \omega}{\hbar(\omega_{ns}^2 - \omega^2)} \right]. \quad (6-10)$$

Using 6-6), 6-8) can be rewritten as

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) + \alpha_{\alpha\alpha'} E_{\alpha'}(t) + \alpha'_{\alpha\alpha'} \frac{\dot{E}_{\alpha'}(t)}{\omega} + \dots \quad (6-11)$$

When $\omega_{ns} \gg \omega$, 6-9) expresses the static electric dipole polarizability.

The electric dipole moment in the presence of a dynamic magnetic field $H_{\alpha'}(t)$ can be evaluated in the same way. In this case, the perturbation analogous to 6-4) is written as

$$H_1(t) = -m_{\alpha'} H_{\alpha'}(t), \quad (6-12)$$

where m is the magnetic dipole moment. Then the time dependent electric dipole moment can be obtained analogously to 6-11) as

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) + G_{\alpha\alpha'} H_{\alpha'}(t) + G'_{\alpha\alpha'} \frac{\dot{H}_{\alpha'}(t)}{\omega} + \dots \quad (6-13)$$

In this equation, $G_{\alpha\alpha'}$ and $G'_{\alpha\alpha'}$ are the frequency dependent electric dipole-magnetic dipole polarizabilities, which are expressed as

$$G_{\alpha\alpha'} = \text{Re} \left[\sum_{n \neq s} \frac{2\mu_{\alpha,sn} m_{\alpha',ns} \omega_{ns}}{\hbar(\omega_{ns}^2 - \omega^2)} \right], \quad (6-14)$$

$$G'_{\alpha\alpha'} = \text{Im} \left[-\sum_{n \neq s} \frac{2\mu_{\alpha,sn} m_{\alpha',ns} \omega}{\hbar(\omega_{ns}^2 - \omega^2)} \right]. \quad (6-15)$$

The magnetic dipole moment in the presence of the dynamic electric field can also be expressed by using $G_{\alpha\alpha'}$ and $G_{\alpha\alpha'}$ as

$$m_{\alpha}(t) = m_{\alpha}(0) + G_{\alpha\alpha'} E_{\alpha'}(t) - G'_{\alpha\alpha'} \frac{\dot{E}_{\alpha'}(t)}{\omega} + \dots \quad (6-16)$$

When both electric and magnetic fields are taken into account, 6-11) and 6-13) must be summed up, therefore

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) + \alpha_{\alpha\alpha'} E_{\alpha'}(t) + \alpha'_{\alpha\alpha'} \frac{\dot{E}_{\alpha'}(t)}{\omega} + G_{\alpha\alpha'} H_{\alpha'}(t) + G'_{\alpha\alpha'} \frac{\dot{H}_{\alpha'}(t)}{\omega} + \dots \quad (6-17)$$

Thus, the general expression for any molecular property $P_{\alpha}(t)$ under the influence of time dependent electric and magnetic fields can be obtained as follows,

$$P_{\alpha}(t) = P_{\alpha}(0) + S_{\alpha\alpha'} E_{\alpha'}(t) + S'_{\alpha\alpha'} \frac{\dot{E}_{\alpha'}(t)}{\omega} + T_{\alpha\alpha'} H_{\alpha'}(t) + T'_{\alpha\alpha'} \frac{\dot{H}_{\alpha'}(t)}{\omega} + \dots, \quad (6-18)$$

where

$$S_{\alpha\alpha'} = \text{Re} \left[\sum_{n \neq s} \frac{2P_{\alpha,sn} \mu_{\alpha',ns} \omega_{ns}}{\hbar (\omega_{ns}^2 - \omega^2)} \right], \quad 6-19$$

$$S'_{\alpha\alpha'} = \text{Im} \left[- \sum_{n \neq s} \frac{2P_{\alpha,sn} \mu_{\alpha',ns} \omega}{\hbar (\omega_{ns}^2 - \omega^2)} \right], \quad 6-20$$

$$T_{\alpha\alpha'} = \text{Re} \left[\sum_{n \neq s} \frac{2P_{\alpha,sn} m_{\alpha',ns} \omega_{ns}}{\hbar (\omega_{ns}^2 - \omega^2)} \right], \quad 6-21$$

$$T'_{\alpha\alpha'} = \text{Im} \left[- \sum_{n \neq s} \frac{2P_{\alpha,sn} m_{\alpha',ns} \omega}{\hbar (\omega_{ns}^2 - \omega^2)} \right]. \quad 6-22$$

In these equations, $P_{\alpha,sn}$ is defined by $P_{\alpha,sn} = \langle \Psi_s^0 | P_\alpha | \Psi_n^0 \rangle$ so as to express the molecular property with the appropriate operator P_α . Using 6-18), the electric quadrupole moment $\theta_{\alpha\beta}(t)$ in the presence of dynamic electric field is given as

$$\theta_{\alpha\beta}(t) = \theta_{\alpha\beta}(0) + A_{\alpha\beta\alpha'} E_{\alpha'}(t). \quad 6-23$$

In 6-23), $A_{\alpha\beta\alpha'}$ is the electric dipole-electric quadrupole polarizability, and is expressed as

$$A_{\alpha\beta\alpha'} = \text{Re} \left\{ \sum_{n \neq s} \frac{2\theta_{\alpha\beta,sn} \mu_{\alpha',ns} \omega_{ns}}{\hbar (\omega_{ns}^2 - \omega^2)} \right\}, \quad 6-24$$

where $\theta_{\alpha\beta,sn} = \langle \Psi_s^0 | \theta_{\alpha\beta} | \Psi_n^0 \rangle$. Noting that the real values of $\theta_{\alpha\beta,sn} \mu_{\alpha',ns}$ and $\mu_{\alpha',sn} \theta_{\alpha\beta,ns}$ are equal, 6-23) and 6-24) can also be written as

$$\theta_{\alpha\beta}(t) = \theta_{\alpha\beta}(0) + A_{\alpha'\alpha\beta} E_{\alpha'}(t), \quad 6-25$$

$$A_{\alpha'\alpha\beta} = \text{Re} \left\{ \sum_{n \neq s} \frac{2\mu_{\alpha',sn} \theta_{\alpha\beta,ns} \omega_{ns}}{\hbar (\omega_{ns}^2 - \omega^2)} \right\}. \quad 6-26$$

Raman optical activities are determined by the changes in molecular electric dipole-electric dipole polarizability $\alpha_{\alpha\beta}$, electric dipole-magnetic dipole polarizability $G'_{\alpha\beta}$ and electric dipole-electric quadrupole polarizability $A_{\alpha\beta\gamma}$, during the molecular vibration. The changes in $\alpha_{\alpha\beta}$ also determines the Raman activities, however, the changes in $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ are unique to ROA.

ROA measurements can be carried out in different experimental geometries. The right angle, back and forward scatterings are those where the angle between the incident and scattering lights is 90° , 180° , and 0° , respectively. When the incident monochromatic light is modulated to the right and left circular polarization states, and the synchronous difference in the Raman scattering is detected, the configuration is referred to as the incident circular polarization (ICP) modulation method. In the ICP method with 90° scattering geometry, the differences for the scattered light with polarization parallel and perpendicular to the scattering plane (the yz -plane) are called as depolarized and polarized ROA scattering, respectively.

When the incident light is linearly polarized, and the intensity difference associated with the right and left circular polarization states of the scattered Raman light is measured, this configuration is referred to as the scattered circular polarization (SCP) modulation method. When the intensity difference associated with the right and left circular polariza-

tion states of the scattered Raman light is measured, with in- or out-of-phase circular polarization state for the incident radiation, the configuration is referred to as the dual circular polarization I (DCP_I) or the dual circular polarization II (DCP_{II}) modulation method.

ROA intensity is expressed as

$$I_{\alpha}^{\zeta} - I_{\beta}^{\delta} \propto \frac{(\nu \mp \nu_a)^4}{\pm 1 \mp \exp\left(\mp \frac{2\pi\nu_a \hbar}{kT}\right)} \cdot \frac{\hbar}{4\pi c^4 \nu_a} \cdot P_{\alpha}, \quad (6-27)$$

where ν is the frequency of incident light, ν_a is the frequency corresponding to a th normal mode, k is the Boltzmann constant and T is the temperature of the sample. I_{α}^{ζ} and I_{β}^{δ} express the intensity of the scattered Raman light, where the superscripts and the subscripts represent the polarization states of incident and scattered light, respectively. P_{α} is called the Raman optical activity, and its value depends on both the measurement type and the scattering geometry. As we have mentioned before, Raman optical activities depend on the changes in molecular electric dipole-electric dipole polarizability $\alpha_{\alpha\beta}$, electric dipole-magnetic dipole polarizability $G'_{\alpha\beta}$ and electric dipole-electric quadrupole polarizability $A_{\alpha\beta\gamma}$, during the molecular vibration. Table 6-1 shows the expressions for the Raman optical activities, P_{α} . These activities involve the terms containing the following quantities.

$$\bar{\alpha}_a = \frac{1}{3} \left(\frac{\partial \alpha_{xx}}{\partial Q_a} + \frac{\partial \alpha_{yy}}{\partial Q_a} + \frac{\partial \alpha_{zz}}{\partial Q_a} \right), \quad (6-28)$$

Table 6-1 Expressions for Raman optical activities

measurement type	scattering geometry	Raman optical activity, P_{α}
$I_x^R - I_x^L, I_R^u - I_L^u$	90°	$\frac{24}{c} \frac{\omega}{\omega} \left(\frac{1}{\omega} \gamma_a^2 - \frac{1}{3\omega} \delta_a^2 \right)$
$I_R^R - I_L^L$	90°	$\frac{4}{c} \frac{\omega}{\omega} \left(\frac{45}{\omega} \bar{\alpha}_a G'_a + \frac{13}{\omega} \gamma_a^2 - \frac{1}{\omega} \delta_a^2 \right)$
$I_x^R - I_x^L, I_R^x - I_L^x$	90°	$\frac{4}{c} \frac{\omega}{\omega} \left(\frac{45}{\omega} \bar{\alpha}_a G'_a + \frac{7}{\omega} \gamma_a^2 - \frac{1}{\omega} \delta_a^2 \right)$
$I_*^R - I_*^L, I_*^* - I_*^*$	90°	$\frac{40}{3c} \frac{\omega}{\omega} \left(\frac{9}{\omega} \bar{\alpha}_a G'_a + \frac{2}{\omega} \gamma_a^2 \right)$
$I_u^R - I_u^L, I_R^u - I_L^u$	180°	$\frac{96}{c} \frac{\omega}{\omega} \left(\frac{1}{\omega} \gamma_a^2 - \frac{1}{3\omega} \delta_a^2 \right)$
$I_R^R - I_L^L$	180°	$\frac{48}{c} \frac{\omega}{\omega} \left(\frac{1}{\omega} \gamma_a^2 - \frac{1}{3\omega} \delta_a^2 \right)$
$I_u^R - I_u^L, I_R^u - I_L^u$	0°	$\frac{16}{c} \frac{\omega}{\omega} \left(\frac{45}{\omega} \bar{\alpha}_a G'_a + \frac{1}{\omega} \gamma_a^2 - \frac{1}{\omega} \delta_a^2 \right)$
$I_R^R - I_L^L$	0°	$\frac{16}{c} \frac{\omega}{\omega} \left(\frac{45}{\omega} \bar{\alpha}_a G'_a + \frac{1}{\omega} \gamma_a^2 - \frac{1}{\omega} \delta_a^2 \right)$

R: right circularly polarized light; *L*: left circularly polarized light; *: magic angle (35.3°); *u*: unpolarized; *x*, *y*, *z*: linear polarization along these axes. Note that in 90° geometry, the incident light is considered to be propagating along *z*-axis, and the scattered light is observed along *y*-axis, with the sample placed at the origin **O**.

$$\begin{aligned}
\gamma_a^2 = & \frac{1}{2} \left[\left(\frac{\partial \alpha_{xx}}{\partial Q_a} - \frac{\partial \alpha_{yy}}{\partial Q_a} \right) \left(\frac{\partial G'_{xx}}{\partial Q_a} - \frac{\partial G'_{yy}}{\partial Q_a} \right) + \left(\frac{\partial \alpha_{yy}}{\partial Q_a} - \frac{\partial \alpha_{zz}}{\partial Q_a} \right) \left(\frac{\partial G'_{yy}}{\partial Q_a} - \frac{\partial G'_{zz}}{\partial Q_a} \right) \right. \\
& + \left. \left(\frac{\partial \alpha_{zz}}{\partial Q_a} - \frac{\partial \alpha_{xx}}{\partial Q_a} \right) \left(\frac{\partial G'_{zz}}{\partial Q_a} - \frac{\partial G'_{xx}}{\partial Q_a} \right) \right. \\
& + 3 \left\{ \frac{\partial \alpha_{xy}}{\partial Q_a} \left(\frac{\partial G'_{xy}}{\partial Q_a} + \frac{\partial G'_{yx}}{\partial Q_a} \right) + \frac{\partial \alpha_{yz}}{\partial Q_a} \left(\frac{\partial G'_{yz}}{\partial Q_a} + \frac{\partial G'_{zy}}{\partial Q_a} \right) \right. \\
& \left. \left. + \frac{\partial \alpha_{zx}}{\partial Q_a} \left(\frac{\partial G'_{zx}}{\partial Q_a} + \frac{\partial G'_{xz}}{\partial Q_a} \right) \right\} \right], \quad 6-29
\end{aligned}$$

$$\begin{aligned}
\delta_a^2 = & \frac{1}{2} \omega \left\{ - \left(\frac{\partial \alpha_{xx}}{\partial Q_a} - \frac{\partial \alpha_{yy}}{\partial Q_a} \right) \frac{\partial A_{xyy}}{\partial Q_a} - \left(\frac{\partial \alpha_{yy}}{\partial Q_a} - \frac{\partial \alpha_{zz}}{\partial Q_a} \right) \frac{\partial A_{xyz}}{\partial Q_a} - \left(\frac{\partial \alpha_{zz}}{\partial Q_a} - \frac{\partial \alpha_{xx}}{\partial Q_a} \right) \frac{\partial A_{yzx}}{\partial Q_a} \right. \\
& + \frac{\partial \alpha_{xy}}{\partial Q_a} \left(\frac{\partial A_{yyz}}{\partial Q_a} - \frac{\partial A_{zyy}}{\partial Q_a} + \frac{\partial A_{zxx}}{\partial Q_a} - \frac{\partial A_{xxz}}{\partial Q_a} \right) \\
& + \frac{\partial \alpha_{yz}}{\partial Q_a} \left(\frac{\partial A_{zxx}}{\partial Q_a} - \frac{\partial A_{xzz}}{\partial Q_a} + \frac{\partial A_{xyy}}{\partial Q_a} - \frac{\partial A_{yyx}}{\partial Q_a} \right), \\
& \left. + \frac{\partial \alpha_{zx}}{\partial Q_a} \left(\frac{\partial A_{xyy}}{\partial Q_a} - \frac{\partial A_{yxx}}{\partial Q_a} + \frac{\partial A_{yzz}}{\partial Q_a} - \frac{\partial A_{zzy}}{\partial Q_a} \right) \right\}. \quad 6-30
\end{aligned}$$

$$\overline{\alpha_a G_a} = \frac{1}{9} \left(\frac{\partial \alpha_{xx}}{\partial Q_a} + \frac{\partial \alpha_{yy}}{\partial Q_a} + \frac{\partial \alpha_{zz}}{\partial Q_a} \right) \left(\frac{\partial G'_{xx}}{\partial Q_a} + \frac{\partial G'_{yy}}{\partial Q_a} + \frac{\partial G'_{zz}}{\partial Q_a} \right). \quad 6-31$$

The experimental ROA intensities depend on the exciting frequency and the incident laser power. Furthermore, the instrumental response needs to be taken into account. To avoid these difficulties, a normalized circular intensity differential (CID) is used to express the experimental quantities. CID is written as

$$\Delta = \frac{I'_a - I''_a}{I'_a + I''_a}. \quad 6-32$$

The expressions for Δ corresponding to different experimental arrangements are obtained as follows. In these expressions, β_a^2 is the anisotropy of the poralizability derivative tensor given as

$$\begin{aligned}
\beta_a^2 = & \frac{1}{2} \left\{ \left(\frac{\partial \alpha_{xx}}{\partial Q_a} - \frac{\partial \alpha_{yy}}{\partial Q_a} \right)^2 + \left(\frac{\partial \alpha_{yy}}{\partial Q_a} - \frac{\partial \alpha_{zz}}{\partial Q_a} \right)^2 + \left(\frac{\partial \alpha_{zz}}{\partial Q_a} - \frac{\partial \alpha_{xx}}{\partial Q_a} \right)^2 \right\} \\
& + 3 \left\{ \left(\frac{\partial \alpha_{xy}}{\partial Q_a} \right)^2 + \left(\frac{\partial \alpha_{yz}}{\partial Q_a} \right)^2 + \left(\frac{\partial \alpha_{zx}}{\partial Q_a} \right)^2 \right\}. \quad 6-33
\end{aligned}$$

(a) Right Angle Scattering

In this case, the incident light is considered to be propagating along z -axis, and the scattered light is observed along y -axis, with the sample placed at the origin \mathbf{O} .

ICP Modulation

Depolarized ROA

$$\Delta(90, R, L, z, z) = \frac{I_z^R - I_z^L}{I_z^R + I_z^L} = \frac{2/c \cdot 8 \cdot (\gamma^2 - \delta^2/3)}{8\beta^2}. \quad 6-34$$

Polarized ROA

$$\Delta(90, R, L, x, x) = \frac{I_x^R - I_x^L}{I_x^R + I_x^L} = \frac{2/c \cdot 4/3 \cdot (45\bar{\alpha}G' + 7\gamma^2 + \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-35$$

Unpolarized ROA

$$\Delta(90, R, L, u, u) = \frac{I_u^R - I_u^L}{I_u^R + I_u^L} = \frac{2/c \cdot 4/3 \cdot (45\bar{\alpha}G' + 13\gamma^2 - \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 13\beta^2)}. \quad 6-36$$

Other Form

$$\Delta(90, R, L, xz, xz) = \frac{(I_x^R - I_x^L) - (I_z^R - I_z^L)}{(I_x^R - I_x^L) + (I_z^R - I_z^L)} = \frac{2/c \cdot 8/3 \cdot (45\bar{\alpha}G' + \gamma^2 + 3\delta^2)}{8/3 \cdot (45\bar{\alpha}^2 + \beta^2)}. \quad 6-37$$

SCP Modulation

$$\Delta(90, y, y, R, L) = \frac{I_R^y - I_L^y}{I_R^y + I_L^y} = \frac{2/c \cdot 8 \cdot (\gamma^2 - \delta^2/3)}{8\beta^2}. \quad 6-38$$

$$\Delta(90, x, x, R, L) = \frac{I_R^x - I_L^x}{I_R^x + I_L^x} = \frac{2/c \cdot 4/3 \cdot (45\bar{\alpha}G' + 7\gamma^2 + \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-39$$

DCP Modulation

$$\Delta(90, R, L, R, L) = \frac{I_R^R - I_L^L}{I_R^R + I_L^L} = \frac{2/c \cdot 4/3 \cdot (45\bar{\alpha}G' + 13\gamma^2 - \delta^2)}{2/3 \cdot (45\bar{\alpha}^2 + 13\beta^2)}. \quad 6-40$$

$$\Delta(90, R, L, L, R) = \frac{I_R^L - I_L^R}{I_R^L + I_L^R} = 0. \quad 6-41$$

$$\Delta(90, R, L, R, R) = \frac{I_R^R - I_R^L}{I_R^R + I_R^L} = \frac{2/c \cdot 2/3 \cdot (45\bar{\alpha}G' + 13\gamma^2 - \delta^2)}{2/3 \cdot (45\bar{\alpha}^2 + 13\beta^2)}. \quad 6-42$$

$$\Delta(90, R, R, R, L) = \frac{I_R^R - I_L^R}{I_R^R + I_L^R} = \frac{2/c \cdot 2/3 \cdot (45\bar{\alpha}G' + 13\gamma^2 - \delta^2)}{2/3 \cdot (45\bar{\alpha}^2 + 13\beta^2)}. \quad 6-43$$

(b) Back Scattering

ICP Modulation

$$\Delta(180, R, L, u, u) = \frac{I_u^R - I_u^L}{I_u^R + I_u^L} = \frac{2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-44$$

SCP Modulation

$$\Delta(180, u, u, R, L) = \frac{I_R^u - I_L^u}{I_R^u + I_L^u} = \frac{2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-45$$

DCP Modulation

$$\Delta(180, R, L, R, L) = \frac{I_R^R - I_L^L}{I_R^R + I_L^L} = \frac{2/c \cdot 32/3 \cdot (3\gamma^2 + \delta^2)}{4/3 \cdot 12\beta^2}. \quad 6-46$$

$$\Delta(180, R, L, L, R) = \frac{I_L^R - I_R^L}{I_L^R + I_R^L} = \frac{0}{8/3 \cdot (45\bar{\alpha}^2 + \beta^2)}. \quad 6-47$$

$$\Delta(180, R, L, R, R) = \frac{I_R^R - I_R^L}{I_R^R + I_R^L} = \frac{4/3 \cdot (5\beta^2 - 45\bar{\alpha}^2) + 2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2)}{2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2) + 4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-48$$

$$\Delta(180, R, R, R, L) = \frac{I_R^R - I_L^R}{I_R^R + I_L^R} = \frac{4/3 \cdot (5\beta^2 - 45\bar{\alpha}^2) + 2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2)}{2/c \cdot 16/3 \cdot (3\gamma^2 + \delta^2) + 4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-49$$

(c) Forward Scattering

ICP Modulation

$$\Delta(0, R, L, u, u) = \frac{I_u^R - I_u^L}{I_u^R + I_u^L} = \frac{2/c \cdot 8/3 \cdot (45\bar{\alpha}\bar{G} + \gamma^2 - \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-50$$

SCP Modulation

$$\Delta(0, u, u, R, L) = \frac{I_R^u - I_L^u}{I_R^u + I_L^u} = \frac{2/c \cdot 8/3 \cdot (45\bar{\alpha}\bar{G} + \gamma^2 - \delta^2)}{4/3 \cdot (45\bar{\alpha}^2 + 7\beta^2)}. \quad 6-51$$

DCP Modulation

$$\Delta(0, R, L, R, L) = \frac{I_R^R - I_L^L}{I_R^R + I_L^L} = \frac{2/c \cdot 16/3 \cdot (45\bar{\alpha}\bar{G} + \gamma^2 - \delta^2)}{8/3 \cdot (45\bar{\alpha}^2 + \beta^2)}. \quad 6-52$$

$$\Delta(0, R, L, L, R) = \frac{I_L^R - I_R^L}{I_L^R + I_R^L} = \frac{0}{16\beta^2}. \quad 6-53$$

These CIDs, however, are not usually reported, and the theoretical ROA intensity is calculated by using 6-27).

VII. Some Examples of ROA Spectra

An ROA apparatus made by BioTools Inc. in USA has been installed in our laboratory on early December in 2003. This is the second machine commercially available in the world

and the first in Japan. The examples of measurements are still limited and the detail interpretations of the spectra are the project in near future. The followings are, therefore, very preliminary results.

Fig. 9 shows the comparison of four types of vibrational spectra of (*R*)-Carvone. The ROA spectrum of liquid sample was measured in 5mm ϕ liquid cell. The wavelength of the exciting laser is 532 nm from a solid semiconductor laser. The laser power is about 300 mW, and 3000 shots in 30 minutes elapsed time.

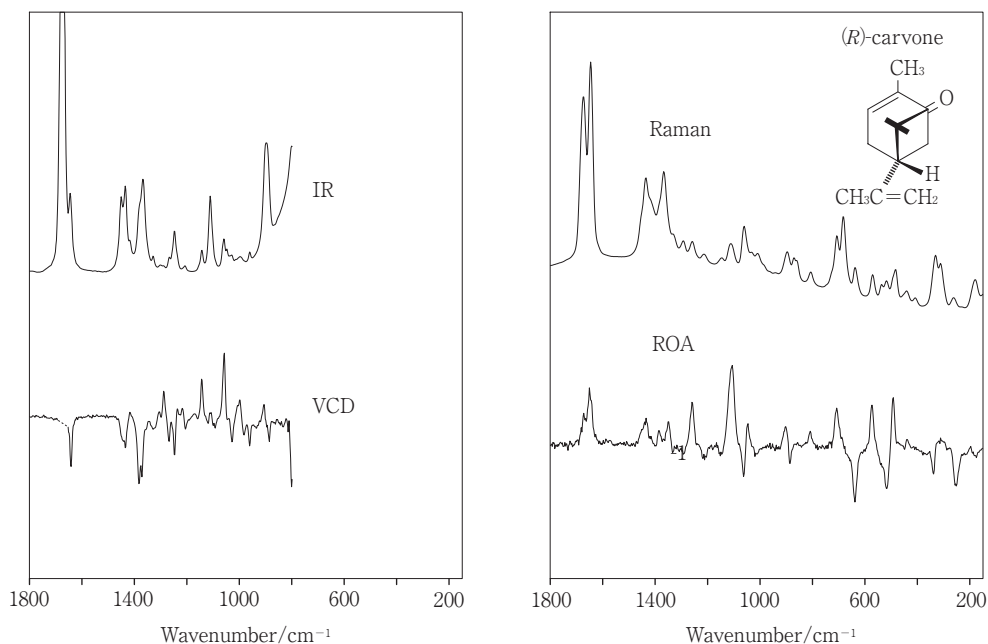


Fig.9 IR, VCD, Raman, and ROA spectra of (*R*)-Carvone
All spectra were measured as a neat sample.

In a relatively short time, a beautiful ROA spectrum was obtained. However, as experienced in VCD spectra^{1,2)} of other molecules, there is no apparent relation between the intensity of Raman band and that of ROA signal. Other than the relation of intensities, the vibrational mode for such a compound where more than two rings are combined back on each other is still unresolved problem in vibrational spectroscopy. Therefore, the detail understanding of this molecule should be postponed for a certain time. On the other hand, according to the information, the coming new version of Gaussian program package will install an option to calculate ROA spectrum. Then, in the not-so-distant future, the ROA spectroscopy will become a useful analytical method for chiral molecules.

We measured and analyzed the infrared and VCD spectrum and found that the OH bend-

ing mode appears in dilute sample and gives fairly strong VCD signal, and stressed the VCD spectroscopy might be a useful tool to investigate the hydrogen bonded system in solution³. We also interpreted the magnitudes and signs of VCD signals in terms of vibrational modes⁴, which will be meaningful in predicting and interpreting the VCD spectra of the other molecules. Considering that Raman spectroscopy is a complementary method to infrared spectroscopy, comparison of VCD and ROA spectra should be instructive.

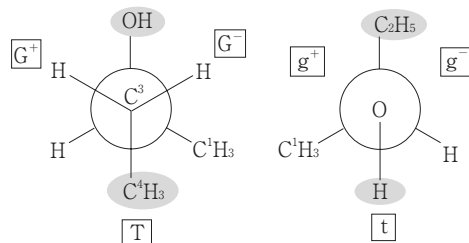


Fig.10 Definitions of rotational isomers of (*S*)-2-butanol

The molecule, 2-butanol, has 9 rotational isomers and its conformers are defined in Fig. 10. Each of their molecular structure was optimized by a theoretical method at B3LYP/6-31++G** level using Gaussian 98 program⁵. The calculated Raman spectra of 9 conformers are shown in Fig. 11, where the population abundance is decreasing from top to bottom.

Fig. 12 shows Raman and ROA spectra of several 2-alcohols different in the lengths of alkyl chains. We will compare these spectra in the following discussions relating with molecular structure and vibrational modes.

In our previous report², we described that the infrared and VCD spectra are roughly classified according to the conformations due to the internal rotation angle of OH group, that is designated by small letters in Fig. 11 such as t, g⁺, or g⁻. On the other hand, Raman spectra seem to be grouped according to the large letters in Fig. 11, that is the conformations due to the dihedral angle made by O(H)–C²–C³–C⁴(H₃) bond, or in fact, the skeletal conformation.

Let us look at the molecular structures first. In G⁺-forms, the C¹(H₃)–C–C–C⁴(H₃) skeleton is almost in coplanar and O atom sticks out of the plane. In T-forms, O(H)–C²–C³–C⁴(H₃) skeleton is almost in coplanar and C¹ atom sticks out of the plane. On the other hand, in G⁻-forms, none of five heavy atoms are in coplanar and make a part of globular shape. In other word, the G⁺ and T-forms have more elongated shape and the G⁻-forms have somehow an orbiculate shape. These structural variations will make the vibrational coupling scheme different in the different skeletal conformers.

Next we point out some vibrational mode assignments typical to conformers due to the PED (potential energy distribution) analysis for the calculated spectra.

There are clusters of several bands making relatively strong Raman intensities around

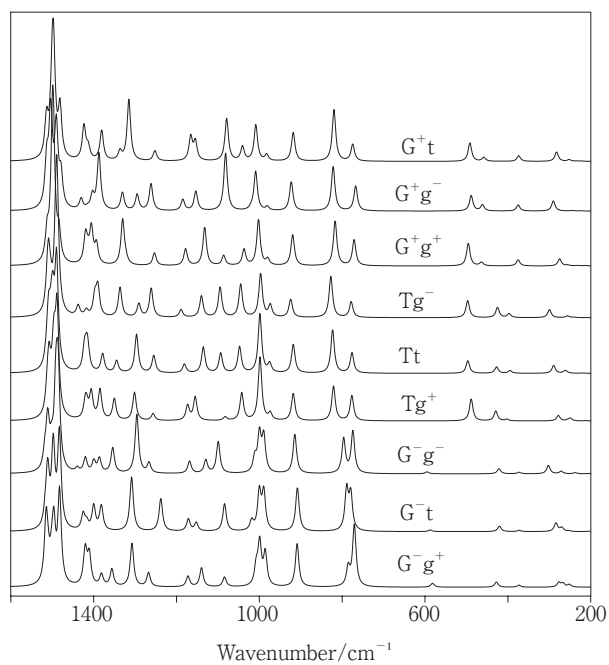


Fig.11 Calculated Raman spectra of various conformers of 2-butanol

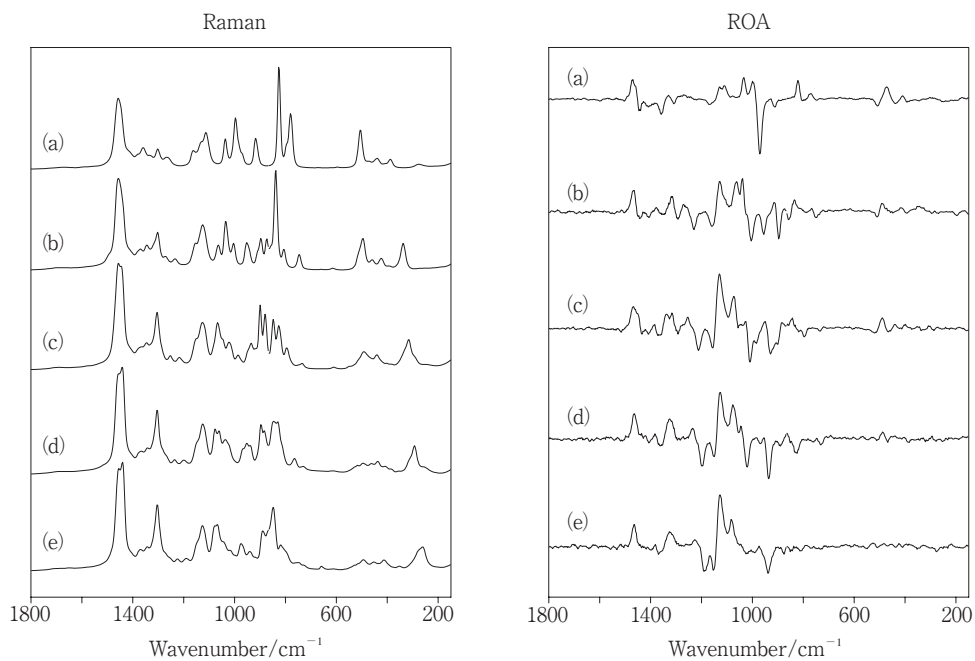


Fig.12 Observed Raman and ROA spectra of 2-alcohols

- (a) (*S*)-2-butanol, (b) (*S*)-2-pentanol, (c) (*S*)-2-hexanol, (d) (*S*)-2-heptanol,
 (e) (*S*)-2-octanol

1500 cm^{-1} , which correspond to the observed bands around 1456 cm^{-1} . There appear positive ROA signals of medium intensities for all alcohols studied in the present work. These ROA signals correspond to the left most bands for every 2-alcohol and they are assigned to C^1H_3 (or CH_3 group attached to chiral carbon) deformation or the terminal CH_3 group of the alkyl chain.

Longer the alkyl chain elongates, stronger becomes the Raman band at around 1300 cm^{-1} as shown in Fig. 12. This band is assigned to the twisting mode of CH_2 group attached to the chiral center in case of 2-butanol. This band becomes more prominent in G^- -forms where the skeletal structure become more orbiculate as described above. This might an indication of such structures for the molecules with longer alkyl chain. This point is worth to investigate in detail. However there is no detectable ROA signals for these bands.

There are negative ROA bands in doublet with strong intensities, which start from the 1229 and 1160 cm^{-1} bands of 2-pentanol down continuously to 1190 cm^{-1} and 1153 cm^{-1} bands of 2-octanol. These bands are assigned to the mixture of various modes, such as CH_3 rocking, $\text{C}-\text{O}$ stretching and so on. The way of mode coupling depends on conformers, and the assignment to a single mode is difficult. These bands have no corresponding strong Raman bands, except the lower frequency bands show a shoulder bands on further lower frequency bands. It is interesting that the lower ones of these two bands show an odd-even effect in their VCD spectra as for the alkyl substituents. The molecules with even number of carbon atoms (i.e. 2-butanol, 2-hexanol, 2-octanol) have strong, positive VCD bands, while the molecules with odd number of carbon atoms (i.e. 2-pentanol, 2-heptanol) have almost no VCD signals.

The Raman band at 1128 cm^{-1} of 2-pentanol and the corresponding bands of the other 2-alcohols except for 2-butanol show about the same intensities and their locations are almost constant. These bands show positive ROA signals and their intensities become far more prominent at higher alkyl chains and in fact these are the strongest ROA bands for 2-hexanol and higher alcohols in the observed region. The corresponding bands of 2-butanol seem to be those at 1127 cm^{-1} and 1112 cm^{-1} . The bands around here are strongly affected by hydrogen bonding, and it is difficult to assign to a single mode.

The positive ROA band at 1034 cm^{-1} of 2-butanol has a medium intensity. The other alcohols have the corresponding bands. Their intensities do not change so much and their locations go to higher frequency a little bit quickly first, then slowly at higher alkyl chains.

It is difficult at this moment to interpret the negative ROA bands between 1000 and 900 cm^{-1} . There is a big gap in continuity for both Raman and ROA spectral pattern between 2-butanol and 2-pentanol. Also we have no ROA signal of 2-octanol at around 1030 cm^{-1} as expected from the other 2-alcohols with shorter alkyl chains. Of course, the vibrational modes of the finger print region is so complicated such that many local coordinates are mixed up and it is almost impossible to describe the normal mode by a simple local coordinate.

According to the PED analysis of the calculated spectra for 2-butanol, the methyl-rocking mode of the terminal CH₃ group is split into two bands. One of them makes a weak shoulder band at 917 cm⁻¹ by mixing with C-C(or C-O) stretching, and the other component makes a strongest band at 827 cm⁻¹ by mixing with CH₂ rocking. The former Raman band turns out to be the strongest negative ROA signal and the latter band turns out to be the medium positive ROA signal. In between the two bands described above, there is an isolated band around 900 cm⁻¹ for every conformer of 2-butanol as shown in Fig. 11. This band is assigned to C-O stretching mode. On the other hand, the bands around 780 cm⁻¹ are assigned to CH₂ rocking mode. The detail investigation of these coupling schemes will be needed to interpret the abnormal spectral behavior in 1000 ~ 800 cm⁻¹ spectral region.

It is interesting to look the change of spectral pattern in 500~200cm⁻¹ spectral region. The medium Raman band at 507 cm⁻¹ of 2-butanol give a negative ROA signal. This band is assigned to skeletal deformation with the chiral carbon atom as an apex. The very weak Raman band at 475 cm⁻¹ of 2-butanol give a positive ROA signal of medium intensity. This band is assigned to the deformation of C¹H₃ group as a whole against the skeletal structure made of O-C-C bond with the chiral carbon atom as a center. These two bands disappear at higher alkyl chains. Instead, a lower frequency band shows up at 338 cm⁻¹ for 2-pentanol, and the frequencies of the corresponding bands decrease at higher alkyl chains. These bands are assigned to the skeletal deformation around the chiral center and C³C⁴C⁵ bending. Unfortunately, there are no ROA signals for these bands.

The descriptions so far made on spectral behavior will be helpful in the analysis of the other molecules. The combined analysis of Raman and ROA spectra will also useful for the interpretation of molecular conformation in solution. As is shown in Fig.12, the Raman and ROA spectra of larger molecules become rather simple regardless of the increased number of the normal vibrations. This is an advantage in the study on large molecular system such as biological molecules if some key bands are in hand. The research for finding such key bands is now at the starting point.

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