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STUDIES ON NATURAL RAMAN OPTICAL ACTIVITY

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Juan R. Escribano

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SUMMARY

Optical activity associated with vibrations of chiral molecules can provide much stereochemical information. There are two techniques which observe vibrational optical activity (VOA), namely: infrared circular dichroism (IRCD) and vibrational Raman optical activity (VROA). The first, IRCD, is an extension of circular dichroism into the infrared and measures a difference in absorbance of incident left and right circularly polarized infrared radiation. VROA is concerned with a difference in the intensity of Raman scattering when the chiral system is illuminated with left and right circularly polarized radiation. Recent reviews that cover both techniques are in the references of the Summary.

This thesis is divided into two main parts. The first (Chapters 1 to 4) is concerned with theoretical studies of ROA. The second (Chapters 5 to 8) with calculations of the observable parameters in VROA and their comparison with experimental results.

Chapter 1 comprises a theoretical study in molecular scattering tensors: one significant new result was the discovery of a Stokes-antiStokes asymmetry in the ROA observables. In Chapter 2 is reviewed the experimental conditions in which VROA experiments have been carried out and how the artifacts will affect their spectra. For this, firstly, it has been necessary to provide a general extension of the established equations which give the ROA observables at any point in space. Subsequently a new and more realistic parameter in ROA is defined in terms of power. The difference with the original one is not important in the experimental conditions in which the spectra are recorded, but it is relevant from the scientific aesthetic point of view. Particular cases are derived from these general equations in total agreement

with the original and well established ones. In all cases the influence of artifacts coming from imperfectly modulated right and left circularly polarized incident light has been considered. Chapter 3 is a generalization of the "two group model" in VROA using the bond polarizability theory. The model has been extended to include deformations of non-axially symmetric groups. A general critical revision of these formulae is provided. Chapter 4 is a survey of miscellanea in VROA. An interesting prediction is given in the case of Fermi resonance. At the end of this chapter a new selection rule is proposed in VROA which relates polarized and depolarized VROA spectra. This rule is analogous to that which relates polarized and depolarized conventional Raman spectra.

The second part of the thesis is devoted to calculations of the observable parameters in VROA and their comparison with the experimental results. The molecule CBrClFH has not yet been studied experimentally but it is a good (Chapter 5) example for calculations because the results can be compared with those from other theories such as the "atom dipole interaction model". Chapter 6 treats another easy chiral molecule, epoxypropane. The advantage of this molecule is that it can be tested with its experimental spectrum and considering the approximate force field we can say that the comparison is good. Chapters 7 and 8 deal with small chiral molecules derived from cyclohexanone, deuterated and methylated. We have included in our calculations two conformers, not just the most stable, and weighting each contribution to the total VROA spectrum. The big couplet centered at 500 cm^{-1} in the (R)-(+)-3-methylcyclohexanone is explained with these considerations. Surprisingly the results do not fit very well in the cases of the deuterated cyclohexanones.

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PART I

1 BASIC SCATTERING RESULTS IN RAMAN OPTICAL ACTIVITY

The theory of molecular light scattering and optical activity is briefly reviewed. It is developed within a semiclassical description of the interaction of radiation and matter in which the molecules are treated with a quantum-mechanical development and the radiation as a classical electromagnetic field. We shall use widely the cartesian tensor notation, from now on, which is essential for manipulating the coupling between electromagnetic field components and the molecular property tensors responsible for the optical activity.

1.1 Molecular multipole moments induced by an electromagnetic wave.

The origin of molecular light scattering is the oscillating electric and magnetic multipole moments induced in a molecule by the incident light wave. The electric dipole moment $\underset{\sim}{\mu}$, magnetic dipole moment $\underset{\sim}{m}$ and electric quadrupole moment $\underset{\sim}{\Theta}$ are defined by (in SI)

$$\mu_\alpha = \sum_i e_i r_{i\alpha} \,, \qquad (1.1.1)$$

$$m_\alpha = \sum_i (e_i/2m_i)\,\varepsilon_{\alpha\beta\gamma}\, r_{i\beta}\, p_{i\gamma} \,, \qquad (1.1.2)$$

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i e_i (3 r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}) \,, \qquad (1.1.3)$$

where particle i at $\underset{\sim}{r}_i$ has a charge e_i, mass m_i and momentum $\underset{\sim}{p}_i$.

The electric and magnetic field vectors of an incident plane-wave light beam of angular frequency ω

traveling in the direction of the unit vector $\underset{\sim}{\mathbf{n}}$ are, in complex notation (denoted by a tilde),

$$\tilde{E}_\alpha = \tilde{E}_\alpha^{(0)} \exp[-i\omega(t - n_\beta r_\beta / c)], \qquad (1.1.4a)$$

$$\tilde{B}_\alpha = \frac{1}{c}\, \varepsilon_{\alpha\beta\gamma}\, n_\beta\, \tilde{E}_\gamma\,. \qquad (1.1.4b)$$

The choice of sign in the exponent of (1.1.4a)is arbitrary since only the real part has physical significance.

The scattered electric field detected in the wave zone at a point d a distance R from the molecular origin is the real part of

$$\tilde{E}_\alpha^d = \frac{\omega^2\mu_0}{4\pi R} \exp[i\omega(R/c - t)]\,[\tilde{\mu}_\alpha^{(0)} - n_\alpha^d\, n_\beta^d\, \tilde{\mu}_\beta^{(0)} - \frac{1}{c}\, \varepsilon_{\alpha\beta\gamma}\, n_\beta^d\, \tilde{m}_\gamma^{(0)}$$

$$- \frac{i\omega}{3c}(n_\beta^d\, \tilde{\textcircled{H}}_{\alpha\beta}^{(0)} - n_\alpha^d\, n_\beta^d\, n_\gamma^d\, \tilde{\textcircled{H}}_{\beta\gamma}^{(0)}) + \dots], \qquad (1.1.5)$$

(Landau and Lifshitz, 1971) where $\underset{\sim}{\mathbf{n}}^d$ is the propagation vector of the detected wave. Since this wave is traveling in the free space between the molecules and are taken as unity and $\underset{\sim}{\mathbf{n}}^d$ is now a unit propagation vector. The complex induced moments are given in terms of the dynamic molecular property tensors by (Buckingham and Raab, 1975)

$$\tilde{\mu}_\alpha^{(0)} = (\tilde{\alpha}_{\alpha\beta} + \frac{1}{c}\, \varepsilon_{\gamma\delta\beta}\, n_\delta^i\, \tilde{G}_{\alpha\gamma} + \frac{i\omega}{3c}\, n_\gamma^i\, \tilde{A}_{\alpha\gamma\beta} + \dots)\tilde{E}_\beta^{(0)}, \qquad (1.1.6a)$$

$$\tilde{m}_\alpha^{(0)} = \tilde{g}_{\alpha\beta}\tilde{E}_\beta^{(0)} + \dots, \qquad (1.1.6b)$$

$$\tilde{\textcircled{H}}_{\alpha\beta}^{(0)} = \mathcal{A}_{\gamma\alpha\beta}\, \tilde{E}_\gamma^{(0)} + \dots, \qquad (1.1.6c)$$

where $\underset{\sim}{\mathbf{n}}^i$ is the propagation vector of the incident wave. So eq.(1.1.5) can now be written as:

$$\tilde{E}_\alpha^d = \frac{\omega^2\mu_0}{4\pi R} \exp[i\omega(R/c - t)]\, \tilde{a}_{\alpha\beta}\, \tilde{E}_\beta^{(0)}, \qquad (1.1.7)$$

where $\tilde{a}_{\alpha\beta}$ is a scattering tensor for particular incident and scattered directions:

$$\tilde{a}_{\alpha\beta} = \tilde{\alpha}_{\alpha\beta} + \frac{i\omega}{3c}\left(n^{i}_{\gamma}\tilde{A}_{\alpha\gamma\beta} - n^{d}_{\gamma}\tilde{\mathcal{A}}_{\beta\gamma\alpha}\right) + \frac{1}{c}\left(\varepsilon_{\gamma\delta\beta}n^{i}_{\delta}\tilde{G}_{\alpha\gamma} + \varepsilon_{\gamma\delta\alpha}n^{d}_{\delta}\tilde{g}_{\gamma\beta}\right) \tag{1.1.8}$$

Not included are the terms in $n^{d}_{\alpha}n^{d}_{\beta}\tilde{\mu}_{\beta}^{(o)}$ and $n^{d}_{\alpha}n^{d}_{\beta}\tilde{\Theta}_{\beta\gamma}^{(o)}$ from (1.1.5) that ensure that the wave is transverse since we only take transverse components of (1.1.7) in subsequent calculations.

We have used the complex notation

$$\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - i\,\alpha'_{\alpha\beta} = \tilde{\alpha}^{*}_{\beta\alpha}, \tag{1.1.9a}$$

$$\tilde{G}_{\alpha\beta} = G_{\alpha\beta} - i\,G'_{\alpha\beta}, \tag{1.1.9b}$$

$$\tilde{A}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} - i\,A'_{\alpha\beta\gamma} = \tilde{A}_{\alpha\gamma\beta}, \tag{1.1.9c}$$

$$\tilde{g}_{\alpha\beta} = G_{\beta\alpha} + i\,G'_{\beta\alpha}, \tag{1.1.9d}$$

$$\tilde{\mathcal{A}}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} + i\,A'_{\alpha\beta\gamma} = \tilde{\mathcal{A}}_{\alpha\gamma\beta}. \tag{1.1.9e}$$

The quantum-mechanical expressions for the dynamic molecular distortion tensors (1.1.9a-e) can be obtained by taking the expectation values of the multipole moment operators using molecular wavefunctions perturbed by the light wave (Buckingham, 1967)

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^{2}-\omega^{2}}\,\mathrm{Re}\left(\langle n|\mu_{\alpha}|j\rangle\langle j|\mu_{\beta}|n\rangle\right) = \alpha_{\beta\alpha}, \tag{1.1.10a}$$

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^{2}-\omega^{2}}\,\mathrm{Im}\left(\langle n|\mu_{\alpha}|j\rangle\langle j|\mu_{\beta}|n\rangle\right) = -\alpha'_{\beta\alpha}, \tag{1.1.10b}$$

$$G_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^{2}-\omega^{2}}\,\mathrm{Re}\left(\langle n|\mu_{\alpha}|j\rangle\langle j|m_{\beta}|n\rangle\right), \tag{1.1.10c}$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega^2}{\omega_{jn}^2-\omega^2}\,\mathrm{Im}\left(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle\right), \qquad (1.1.10d)$$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}^2}{\omega_{jn}^2-\omega^2}\,\mathrm{Re}\left(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle\right) = A_{\alpha\gamma\beta}\;, \qquad (1.1.10e)$$

$$A'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega^2}{\omega_{jn}^2-\omega^2}\,\mathrm{Im}\left(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle\right) = A'_{\alpha\gamma\beta}\;, \qquad (1.1.10f)$$

where $\omega_{jn} = \omega_j - \omega_n$, and $|n\rangle$ and $|j\rangle$ are the ground and j-th excited molecular states.

The symmetric polarizability $\alpha_{\alpha\beta}$ provides the major contribution to light scattering and refraction and, since the real part of a product of electric dipole transition moments is specified, it is supported by all molecules. In the antisymmetric polarizability $\alpha'_{\alpha\beta}$, the imaginary part of a product of electric dipole transition moments is specified; this means that, since μ_α is real, $\alpha'_{\alpha\beta}$ is supported only by systems for which the unique wavefunctions are complex. The scalar part of the tensor $G'_{\alpha\beta}$ is familiar from the Rosenfeld equation (Rosenfeld, 1928), in which the natural optical rotation of isotropic samples is proportional to $G'_{\alpha\alpha}$,and this is supported only by chiral molecules (lacking inversion centers and reflection planes). Although $A_{\alpha\beta\gamma}$ does not contribute to optical rotation of isotropic samples, it provides a contribution of the same order as $G'_{\alpha\beta}$ in oriented samples (Buckingham and Dunn, 1971). The remaining tensors $G_{\alpha\beta}$ and $A'_{\alpha\beta\gamma}$ are only non-zero in systems that are time antisymmetric and generate phenomena such as gyrotropic birefringence (Horneich and Shtrikman, 1968). The polarizability and optical activity tensors (1.1.10a-f) are only valid when the frequency of the incident light is far from one of the natural transition frequencies ω_{jn} of the molecule.

1.2 Molecular scattering transition tensors.

The calculated induced multipole moments are oscillating with the same frequency as, and with a definite phase relation to, the inducing light wave. Radiation from such moments is responsible for Rayleigh scattering. But the Raman components of the scattered waves have frequencies different from, and are unrelated in phase to the incident wave, so the polarizability and optical activity tensors must be replaced by corresponding transition tensors which take account of the different initial and final molecular states. In place of the expectation values of the multipole moment operators, real transition moments between initial and final molecular states $|n'\rangle$ and $|m'\rangle$ perturbed by the light wave,are introduced. For example, the transition electric dipole moment is (Placzek, 1934; Born and Huang, 1954)

$$(\mu_\alpha)_{mn} = \langle m'|\mu_\alpha|n'\rangle + \langle m'|\mu_\alpha|n'\rangle^* \; . \qquad (1.2.1)$$

We can extend this argument for magnetic dipole and electric quadrupole moments as follows

$$(\tilde{\mu}_\alpha)_{mn} = (\tilde{\alpha}_{\alpha\beta})_{mn}\tilde{E}_\beta + (\tilde{G}_{\alpha\beta})_{mn}\tilde{B}_\beta + \tfrac{1}{3}(\tilde{A}_{\alpha\beta\gamma})_{mn}\tilde{E}_{\beta\gamma} + \cdots \, , \qquad (1.2.2a)$$

$$(\tilde{m}_\alpha)_{mn} = (\tilde{\mathcal{G}}_{\alpha\beta})_{mn}\tilde{E}_\beta + \cdots \, , \qquad (1.2.2b)$$

$$(\tilde{\Theta}_{\alpha\beta})_{mn} = (\tilde{\mathcal{A}}_{\gamma\alpha\beta})_{mn}\tilde{E}_\gamma + \cdots \, , \qquad (1.2.2c)$$

where the electric and magnetic fields, $\tilde{E}_\beta$ and $\tilde{B}_\beta$, and the electric field gradients $\tilde{E}_{\beta\gamma}$ are all evaluated at the molecular origin and are functions of the angular frequency $(\omega - \omega_{mn})$ of the Raman wave, ω being the incident frequency and ω_{mn} the Raman transition frequency between the initial, $|n\rangle$, and final, $|m\rangle$, molecular states. When $\omega_m > \omega_n$, $(\omega - \omega_{mn}) < \omega$ and is refered to as Stokes Raman scattering, whereas when $\omega_m > \omega_n$, $(\omega - \omega_{mn}) > \omega$ which corresponds to an antiStokes scattering. The complex transition polarizability and optical activity tensors are obtained from time-dependent perturbation theory (e.g. Barron, 1982) and have the form

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle}{\omega_{jn}-\omega} + \frac{\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm}+\omega}\right] = (\tilde{\alpha}_{\beta\alpha})^*_{nm}, \tag{1.2.3a}$$

$$(\tilde{G}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle}{\omega_{jn}-\omega} + \frac{\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm}+\omega}\right] = (\tilde{\mathcal{G}}_{\beta\alpha})^*_{nm}, \tag{1.2.3b}$$

$$(\tilde{A}_{\alpha\beta\gamma})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle}{\omega_{jn}-\omega} + \frac{\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm}+\omega}\right] = (\tilde{\mathcal{A}}_{\alpha\beta\gamma})^*_{nm}, \tag{1.2.3c}$$

$$(\tilde{\mathcal{G}}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|m_\alpha|j\rangle\langle j|\mu_\beta|n\rangle}{\omega_{jn}-\omega} + \frac{\langle m|\mu_\beta|j\rangle\langle j|m_\alpha|n\rangle}{\omega_{jm}+\omega}\right] = (\tilde{G}_{\beta\alpha})^*_{nm}, \tag{1.2.3d}$$

$$(\tilde{\mathcal{A}}_{\gamma\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\Theta_{\alpha\beta}|j\rangle\langle j|\mu_\gamma|n\rangle}{\omega_{jn}-\omega} + \frac{\langle m|\mu_\gamma|j\rangle\langle j|\Theta_{\alpha\beta}|n\rangle}{\omega_{jm}+\omega}\right] = (\tilde{A}_{\gamma\alpha\beta})^*_{nm}. \tag{1.2.3e}$$

These are generalizations of corresponding tensors introduced by Buckingham and Raab (1975). Writing them explicitly in real and imaginary parts, we have

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = (\alpha_{\alpha\beta})_{mn} - i\,(\alpha'_{\alpha\beta})_{mn}, \tag{1.2.4a}$$

$$(\tilde{G}_{\alpha\beta})_{mn} = (G_{\alpha\beta})_{mn} - i\,(G'_{\alpha\beta})_{mn}, \tag{1.2.4b}$$

$$(\tilde{A}_{\alpha\beta\gamma})_{mn} = (A_{\alpha\beta\gamma})_{mn} - i\,(A'_{\alpha\beta\gamma})_{mn}, \tag{1.2.4c}$$

$$(\tilde{\mathcal{G}}_{\alpha\beta})_{mn} = (\mathcal{G}_{\alpha\beta})_{mn} - i\,(\mathcal{G}'_{\alpha\beta})_{mn}, \tag{1.2.4d}$$

$$(\tilde{\mathcal{A}}_{\gamma\alpha\beta})_{mn} = (\mathcal{A}_{\gamma\alpha\beta})_{mn} - i\,(\mathcal{A}'_{\gamma\alpha\beta})_{mn}. \tag{1.2.4e}$$

The case of $(\tilde{G}_{\alpha\beta})_{mn}$ is

$$(G_{\alpha\beta})_{mn} = \frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}$$
$$\times\left[(\omega_{jn}+\omega_{jm})\,\mathrm{Re}\left(\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle+\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right.$$
$$\left.+\,(2\omega+\omega_{nm})\,\mathrm{Re}\left(\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle-\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right],$$

(1.2.5a)

and

$$(G'_{\alpha\beta})_{mn} = -\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}$$
$$\times\left[(\omega_{jn}+\omega_{jm})\,\mathrm{Im}\left(\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle+\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right.$$
$$\left.+\,(2\omega+\omega_{nm})\,\mathrm{Im}\left(\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle-\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right].$$

(1.2.5b)

Similarly for $(\tilde{g}_{\alpha\beta})_{mn}$ but here μ_α and m_β are replaced everywhere by m_α and μ_β. With respect to $(\tilde{A}_{\alpha\beta\gamma})_{mn}$

$$(A_{\alpha\beta\gamma})_{mn} = \frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}$$
$$\times\left[(\omega_{jn}+\omega_{jm})\,\mathrm{Re}\left(\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle+\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right.$$
$$\left.+\,(2\omega+\omega_{nm})\,\mathrm{Re}\left(\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle-\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right],$$

(1.2.5c)

and

$$(A'_{\alpha\beta\gamma})_{mn} = -\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}$$
$$\times\left[(\omega_{jn}+\omega_{jm})\,\mathrm{Im}\left(\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle+\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right.$$
$$\left.+\,(2\omega+\omega_{nm})\,\mathrm{Im}\left(\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle-\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle\right)\right].$$

(1.2.5d)

For $(\tilde{\mathcal{A}}_{\gamma\alpha\beta})_{mn}$ we should do the changes $\mu_\alpha - \Theta_{\alpha\beta}$ and $\Theta_{\beta\gamma} - \mu_\gamma$. The expressions for the real and imaginary parts of $(\tilde{\alpha}_{\alpha\beta})_{mn}$ can be found elswhere (Barron, 1982).

If m = n (Rayleigh scattering) then (1.2.5) reduce to (1.1.10), as required, and the real part of the complex transition polarizability is then purely symmetric and the imaginary part purely antisymmetric. But when m ≠ n (Raman scattering), both real and imaginary parts of the complex transition polarizability contain symmetric and antisymmetric parts, although these additional parts only contribute to resonance Raman scattering and disappear at transparent frequencies (Placzek, 1934; Barron, 1982). Analogously, for m = n we have for the optical activity tensors from (1.1.9b-e) and (1.2.4b-e)

$$g_{\alpha\beta} = G_{\beta\alpha}\ ,\ g'_{\alpha\beta} = -G'_{\beta\alpha} \quad \text{and} \quad \mathcal{A}_{\gamma\alpha\beta} = A_{\gamma\alpha\beta}\ ,\ \mathcal{A}'_{\gamma\alpha\beta} = -A'_{\gamma\alpha\beta}$$

1.3 Raman scattering mechanisms.

The vibrational Raman transition tensors can be developed in two distinct ways: Placzek's polarizability theory (Placzek, 1934; Born and Huang, 1954), which considers the dependence of the ground state electronic polarizability on the normal coordinates of vibration; and the vibronic expansion theory (Albrecht, 1961; Barron, 1976), which considers the vibrational perturbation of the ground and excited electronic states. The polarizability theory is best for transparent frequencies and the vibronic expansion theory for the resonance situation since ground state theories depend on a formal sum over all excited states.

Let us consider Placzek's theory first. Within the Born-Oppenheimer approximation, a general molecular state is written as a product of rotational, vibrational and electronic parts $|j_{evr}\rangle = |j_e j_v j_r\rangle = |j_e\rangle|j_v\rangle|j_r\rangle$. In what follows we suppress the rotational contributions to the transition frequencies except for the terms with $j_e j_v = n_e n_v = 00$. These terms, which involve pure rotational virtual excited states, will only be significant for incident radiation at microwave frequencies. The general transition tensors (1.2.4) reduce to vibrational transition tensors in which the electronic part of the tensor is regarded as an operator (being a function of the normal vibrational coordinates Q) that brings about the vibrational transitions. Assuming that the initial and final vibrational states $|n_v\rangle$ and $|m_v\rangle$ are real, and no external magnetic field is present, we can write

$$(\tilde{\alpha}_{\alpha\beta})_{mn} \longrightarrow \langle m_v|\alpha_{\alpha\beta}(Q)|n_v\rangle, \tag{1.3.1a}$$

$$(\tilde{G}_{\alpha\beta})_{mn} \longrightarrow -i\langle m_v|G'_{\alpha\beta}(Q)|n_v\rangle, \tag{1.3.1b}$$

$$(\tilde{A}_{\alpha\beta\gamma})_{mn} \longrightarrow \langle m_v|A_{\alpha\beta\gamma}(Q)|n_v\rangle, \tag{1.3.1c}$$

$$(\tilde{\mathcal{G}}_{\alpha\beta})_{mn} \longrightarrow i\langle m_v|G'_{\beta\alpha}(Q)|n_v\rangle, \tag{1.3.1d}$$

$$(\tilde{\mathcal{A}}_{\gamma\alpha\beta})_{mn} \longrightarrow \langle m_v|A_{\gamma\alpha\beta}(Q)|n_v\rangle, \tag{1.3.1e}$$

where

$$\alpha_{\alpha\beta}(Q) = \frac{2}{\hbar}\sum_{j_e\neq n_e}\frac{\omega_{j_e n_e}}{\omega^2_{j_e n_e}-\omega^2}\,\mathrm{Re}\left(\langle n_e|\mu_\alpha|j_e\rangle\langle j_e|\mu_\beta|n_e\rangle\right), \tag{1.3.2a}$$

$$G'_{\alpha\beta}(Q) = -\frac{2}{\hbar}\sum_{j_e\neq n_e}\frac{\omega}{\omega^2_{j_e n_e}-\omega^2}\,\mathrm{Im}\left(\langle n_e|\mu_\alpha|j_e\rangle\langle j_e|m_\beta|n_e\rangle\right), \tag{1.3.2b}$$

$$A_{\alpha\beta\gamma}(Q) = \frac{2}{\hbar}\sum_{j_e\neq n_e}\frac{\omega_{j_e n_e}}{\omega^2_{j_e n_e}-\omega^2}\,\mathrm{Re}\left(\langle n_e|\mu_\alpha|j_e\rangle\langle j_e|\Theta_{\beta\gamma}|n_e\rangle\right). \tag{1.3.2c}$$

In this theory, fundamental vibrational transitions are due to $(\partial\alpha_{\alpha\beta}/\partial Q_p)_0\langle m_v|Q_p|n_v\rangle$,and since in this case $\langle m_v|Q_p|n_v\rangle = \langle n_v|Q_p|m_v\rangle$ it follows that $(\tilde{\alpha}_{\alpha\beta})_{mn} = (\tilde{\alpha}_{\alpha\beta})_{nm}$.The same arguments are valid for optical activity tensors and we shall get the equivalent results. Thus, for vibrational Raman scattering at transparent frequencies Placzek's theory predicts the same values for the tensors in a Stokes and antiStokes transitions.

Now consider the vibronic theory. This is usually based on the Herzberg-Teller approximation in which the electronic states at the equilibrium nuclear configuration are taken to be perturberd by terms describing the dependence of the electronic Hamiltonian H_e on the normal vibrational coordinates:

$$|j_e'\rangle = |j_e\rangle + \hbar^{-1}\sum_{j_e\neq k_e}\frac{\langle k_e|\sum_p(\partial H_e/\partial Q_p)_0 Q_p|j_e\rangle}{\omega_{j_e}-\omega_{k_e}}|k_e\rangle + \cdots \quad .$$

For fundamental vibrational Raman transitions, each product of transition moments in (1.2.3) is written perturberd to first order in $\sum_p (\partial H_e/\partial Q_p)_0 Q_p$. For example,

$$\begin{aligned}
\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle &= \langle m_v m_e'|\mu_\alpha|j_v j_e'\rangle\langle j_v j_e'|m_\beta|n_v n_e'\rangle \\
&= \langle m_e|\mu_\alpha|j_e\rangle\langle j_e|m_\beta|n_e\rangle\langle m_v|j_v\rangle\langle j_v|n_v\rangle \\
&+ \sum_{k_e\neq n_e}\frac{\langle k_e|\sum_p(\partial H_e/\partial Q_p)_0|n_e\rangle}{\hbar\omega_{n_e k_e}}\langle m_e|\mu_\alpha|j_e\rangle\langle j_e|m_\beta|k_e\rangle\langle m_v|j_v\rangle\langle j_v|Q_p|n_v\rangle \\
&+ \sum_{k_e\neq m_e}\frac{\langle k_e|\sum_p(\partial H_e/\partial Q_p)_0|m_e\rangle^*}{\hbar\omega_{m_e k_e}}\langle k_e|\mu_\alpha|j_e\rangle\langle j_e|m_\beta|n_e\rangle\langle m_v|Q_p^*|j_v\rangle\langle j_v|n_v\rangle \\
&+ \sum_{k_e\neq j_e}\frac{\langle k_e|\sum_p(\partial H_e/\partial Q_p)_0|j_e\rangle^*}{\hbar\omega_{j_e k_e}}\langle m_e|\mu_\alpha|j_e\rangle\langle k_e|m_\beta|n_e\rangle\langle m_v|j_v\rangle\langle j_v|Q_p^*|n_v\rangle \\
&+ \sum_{k_e\neq j_e}\frac{\langle k_e|\sum_p(\partial H_e/\partial Q_p)_0|j_e\rangle}{\hbar\omega_{j_e k_e}}\langle m_e|\mu_\alpha|k_e\rangle\langle j_e|m_\beta|n_e\rangle\langle m_v|Q_p|j_v\rangle\langle j_v|n_v\rangle \\
&+ \cdots
\end{aligned}$$

(1.3.3)

These expressions can be applied to both transparent and resonance Raman scattering, both vibrational ($m_e = n_e$) and electronic ($m_e \neq n_e$).

In the application of (1.3.3) to transparent vibrational Raman scattering, a sum is taken over all intermediate states $|j_v j_e\rangle$ and in the assumption that the potential energy surfaces in the ground and excited electronic states are sufficiently similar that the vibrational states in the different electronic levels are orthonormal, $\langle j_v | j_n \rangle = \delta_{j_v\, j_n}$. The vibronic frequency factors ω_{jn} and ω_{jm} in (1.3.3) are replaced by purely electronic factors and the closure theorem invoked in the space of the vibrational wavefunctions so that,

$$\sum_{j_v} \langle m_v | j_v \rangle \langle j_v | n_v \rangle = \langle m_v | n_v \rangle = \delta_{m_v n_v} \ ,$$

$$\sum_{j_v} \langle m_v | j_v \rangle \langle j_v | Q_p | n_v \rangle = \langle m_v | Q_p | n_v \rangle \quad ,$$

$$\sum_{j_v} \langle m_v | Q_p | j_v \rangle \langle j_v | n_v \rangle = \langle m_v | Q_p | n_v \rangle \ .$$

Thus at transparent frequencies the first term contributes only to Rayleigh scattering. Therefore, in this approximation, Raman scattering arises as a result of vibronic coupling and is determined by the remaining terms (Albrecht , 1961; Barron, 1982). So $(\tilde{\alpha}_{\alpha\beta})_{mn} = (\tilde{\alpha}_{\alpha\beta})_{nm}$, etc., as in Placzek's theory refered to above.

In applying (1.3.3) to resonance vibrational Raman scattering ($m_e = n_e$) it is no longer justifiable to replace the vibronic frequency factors by purely electronic factors and to invoke the closure theorem in the space of vibrational states, since the precise values of the $\omega_{j_e j_v\, n_e\, n_v}$ are now critical and the small but finite values of the Franck-Condon overlap integrals (which are taken to be zero at transparent frequencies) can lead to significant effects. The factor $\langle m_v | j_v \rangle \langle j_v | n_v \rangle$ is determined by the magnitude of one or other of the Franck-Condon overlap integrals $\langle m_v | j_v \rangle$ and $\langle j_v | n_v \rangle$ depending or whether $j_v = n_v$ or m_v. Now the first term of (1.3.3) can contribute to Raman scattering in the resonance case. Nevertheless the factors $\langle m_v | j_v \rangle \times \langle j_v | Q_p | n_v \rangle$ and $\langle m_v | Q_p | j_v \rangle \langle j_v | n_v \rangle$ are mainly responsible for the Raman scattering specially when $m_v = n_v \pm 1$. The case of the 0-0 and 0-1 Stokes vibronic absorption transitions and the corresponding 1-0 and 1-1 antiStokes constitute an example of Stokes-antiStokes vibrational Raman asymmetry. (We denote an A-B transition as that from the vibrational state A in the ground electronic level to the vibrational state B in the excited electronic level). Then for pure vibrational Raman scattering ($m_e = n_e$), the differences in (1.3.3) for the Stokes ($m \leftarrow n$) and the corresponding antiStokes transition ($n \leftarrow m$) reside exclusively in the vibrational factors. Since $\langle j_v | n_v \rangle = \langle n_v | j_v \rangle$ and $\langle m_v | j_v \rangle = \langle j_v | m_v \rangle$, it follows that the first term is identical in the two cases, so for this contribution there is no Stokes-antiStokes asymmetry in the resonance ROA observables, such as we shall see later in Section 1.5. But since the magnitudes of $\langle m_v | Q_p | j_v \rangle \langle j_v | n_v \rangle$ and $\langle m_v | j_v \rangle \langle j_v | Q_p | n_v \rangle$ are in general quite different, there will be a Stokes-antiStokes asymmetry in the resonance ROA observables generated by terms containing these factors.

The case of electronic Raman scattering ($m_e \neq n_e$) also can be considered within this context. It is clear that, unless n_e and m_e are components of the same degenerate set, there will always be a Stokes-antiStokes asymmetry in the ROA observables (Section 1.5), even at transparent frequencies, because the electric dipole and magnetic dipole (or electric dipole and electric quadrupole) operators now connect different pairs of electronic states.

1.4 Molecular scattering of circularly polarized light.

The origin of the scattered light can be considered as the radiation of electromagnetic waves by the oscillating electric and magnetic multipoles (1.1.2) induced in the molecule by the incident light wave. The observables in Rayleigh and Raman optical activity are a small circularly polarized component in the scattered light, and a small difference in the scattered intensity in right and left circularly polarized incident light. So far, only the circular intensity difference has been measured. Barron and Buckingham (1971) have developed the theory in terms of the Rayleigh and Raman circular intensity difference (CID) defined by

$$\Delta_a = (I_a^R - I_a^L)/(I_a^R + I_a^L), \qquad (1.4.1)$$

where $I_a^{R,L}$ is the scattered intensity with a-polarization in right (R) and left (L) circularly polarized incident light, this being the chosen experimental quantity. Hug and Surbeck (1979) have introduced the chirality number $q = (d\sigma^L - d\sigma^R)/d\sigma$, where $d\sigma^{R,L}$ are the differential scattering cross sections in left and right circularly polarized incident light at a certain scattering angle. The relationship with Δ is: $q = -2\Delta$. Arguments have been given in favour of each other (Barron and Torrance, 1983; Nafie, 1983). This work will accept the CID parameter following the original theoretical basis of ROA.

Another observable in ROA is the degree ofcircular polarization $P_c(a)$ of the scattered light. The definition is the ratio of the intensity of the circular polarized scattered light divided by the total scattered intensity when the incident light has an a-linear polarization.

$$P_c(a) = S_3^d/S_0^d \, . \qquad (1.4.2)$$

(For the definitions of S_0 and S_3 see Section <u>2.1</u>). The state of the scattered light beam can be characterized by the set of four Stokes parameters corresponding to four intensity measurements. We shall deal with this matter more extensively in Chapter 2. The CIDs can be extracted from these Stokes parameters. In 0° and 180° scattering the total intensity is sampled, whereas in 90° scattering we require components linearly polarized perpendicular ($I_x \propto S_0 + S_1$) and parallel ($I_z \propto S_0 + S_1$) to the scattering plane yz. Thus,

$$\begin{aligned}\Delta(0^\circ) = 4\,\mathrm{Im}\Big[\tfrac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}(\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} - 2\tilde{\alpha}_{\beta\alpha}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) + 6\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta}\\ + \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} + 5\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} - 5\tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\Big]/2c(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha}\\ + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}),\end{aligned} \tag{1.4.3a}$$

$$\begin{aligned}\Delta(180^\circ) = 2\,\mathrm{Im}\Big[\tfrac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}(\tilde{\alpha}_{\beta\alpha}\hat{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\beta\alpha}\hat{\mathcal{A}}^*_{\gamma\delta\beta}) + 6\tilde{\alpha}_{\alpha\beta}\hat{G}^*_{\alpha\beta}\\ + \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} - 5\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} + 5\tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\Big]/c(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\hat{\alpha}^*_{\beta\alpha}\\ + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}),\end{aligned} \tag{1.4.3b}$$

$$\Delta_z(90^\circ) = \frac{4\,\mathrm{Im}(-\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + 4\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\hat{G}^*_{\beta\beta})}{2c(4\hat{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})}, \tag{1.4.3c}$$

$$\Delta_x(90^\circ) = \frac{2\,\mathrm{Im}(\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + 6\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta})}{c(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\hat{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\hat{\alpha}^*_{\beta\beta})}. \tag{1.4.3d}$$

For the degrees of circular polarization we take the case of linearly polarized incident light so as to avoid complications from the conventional reversal ratio in the forward and backward directions that arises using incident circularly polarized light (Placzek, 1934; Barron, 1982). For scattering at right angles we use linearly polarized light perpendicular and parallel to the scattering plane. We find

$$P_c(0^\circ) = 2\,\mathrm{Im}\Big[\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}(-2\tilde{\alpha}_{\alpha\beta}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) - 5\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + 5\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta}$$

$$- 6\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\Big]/c(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}), \quad (1.4.4a)$$

$$P_c(180^\circ) = 2\,\mathrm{Im}\Big[\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}(2\tilde{\alpha}_{\alpha\beta}\tilde{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) + 5\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 5\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta}$$

$$- 6\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\Big]/c(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}), \quad (1.4.4b)$$

$$P_c(90^\circ, x) = \frac{2\,\mathrm{Im}\left(\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} - 6\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\right)}{c\left(6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}\right)}, \quad (1.4.4c)$$

$$P_c(90^\circ, y) = \frac{4\,\mathrm{Im}\left(-\frac{i\omega}{3}\varepsilon_{\alpha\gamma\delta}\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} - 4\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\mathcal{G}}^*_{\beta\beta}\right)}{2c\left(4\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}\right)}, \quad (1.4.4d)$$

The terms in α^2 that depend on $P\cos 2\eta \sin 2\theta$ (2.2.7-9) vanish from time-reversal arguments (since the imaginary parts are specified) (Barron, 1982) in forward and backward scattering.

For economy we have written $(\tilde{\alpha}_{\alpha\beta})_{mn}$ etc. simply as $\tilde{\alpha}_{\alpha\beta}$ etc. . The case of m = n has been implicitly taken in the literature (e.g. Barron, 1982) so all previously published results are not sufficiently general to expose the Stokes-antiStokes asymmetry which is discussed below.

The symmetry requirements for natural Rayleigh optical activity are that the same componentes of $\tilde{\alpha}_{\alpha\beta}$ and $\tilde{G}_{\alpha\beta}$ span the totally symmmetric representation; and for natural vibrational Raman optical activity the same components of $\tilde{\alpha}_{\alpha\beta}$ and $\tilde{G}_{\alpha\beta}$ must span the irreducible representation of the particular normal coordinate of vibration. This can only happen in chiral point groups:

C_n, D_n, O, T and I (which lack improper rotation elements) in which polar and axial tensors of the same rank (such as $\tilde{\alpha}_{\alpha\beta}$, $\tilde{G}_{\alpha\beta}$ and $\varepsilon_{\alpha\gamma\delta}\tilde{A}_{\gamma\delta\beta}$) have indentical transformation properties. Consequently, all the Raman active vibrations in a chiral molecule should show Raman optical activity.

1.5 General relations between Stokes and antiStokes Raman optical activity observables.

The CIDs (1.4.3) and the degrees of circular polarization (1.4.4) look rather different because the former involve only the Roman transition tensor (1.2.3a-c) whereas the latter involve the script tensors (1.2.3a,d,e) as well. Using the relationships (1.2.3a-e) in (1.4.3) and (1.4.4) we find that, quite generally, the CIDs for the Stokes Raman transition $m \leftarrow n$ are precisely equal to the corresponding degrees of circular polarization for the associated antiStokes transition $m \leftarrow n$,

$$[\Delta(0^\circ)]_{mn} = [P_c(0^\circ)]_{nm},$$

$$[\Delta(180^\circ)]_{mn} = [P_c(180^\circ)]_{nm},$$

$$[\Delta_x(90^\circ)]_{mn} = [P_c(90^\circ,x)]_{nm},$$

$$[\Delta_z(90^\circ)]_{mn} = [P_c(90^\circ,y)]_{nm},$$

and *vice-versa*.

On the other hand the Stokes and antiStokes CIDs will, in general be different, as will the Stokes and antiStokes degrees of circular polarization, i.e., $(\Delta)_{mn} \neq (\Delta)_{nm}$ and $(P_c)_{mn} \neq (P_c)_{nm}$. Clearly the condition for the same optical activity observables to be equal in the

Stokes and antiStokes spectrum is that $(\tilde{\alpha}_{\alpha\beta})_{mn} = (\tilde{\alpha}_{\alpha\beta})_{nm}$ etc.. This of course is the case when n = m, corresponding to Rayleigh scattering.

It can be concluded from above that the Stokes CID Δ equals the associated antiStokes degree of circular polarization P_c. But only for *vibrational* Raman scattering at transparent frequencies will the Stokes Δ equal the antiStokes Δ, and the Stokes P_c equal the antiStokes P_c. In *vibrational* *resonance*, and in both *transparent* and *resonance* *electronic* Raman processes there will in general be an asymmetry between the corresponding Stokes and antiStokes observables.

Further discussion requires a consideration of the mechanisms generating natural optical activity (Barron, 1982) and will be confined here to a few general remarks.

The degree of Stokes-antiStokes asymmetry hinges on the relative magnitudes of the electric dipole, magnetic dipole and electric quadrupole transition moments between the initial, intermediate and final electronic states involved in the scattering pathway. These relative magnitudes are determined in large part by which components are allowed and which forbidden in the corresponding achiral parent molecule with which the chiral molecule can often be correlated: for example, the selection rules in the chiral D_3 complex $[Co(en)_3]^{3+}$ are predominantly those of the parent O_h complex $[Co(NH_3)_6]^{3+}$ (MacCaffery and Mason, 1963).

Consider first the limit of an electronic Raman process in which the incident frequency is in resonance with an excited electronic state $|j_e\rangle$ that can only be reached from the initial state $|n_e\rangle$ by a magnetic dipole transition, and can only connect with the final state $|m_e\rangle$ by an electric dipole transition, in the parent achiral molecule. Since the second terms of the transition tensors (1.2.3) can be neglected at resonance, it can be seen from the first terms of (1.2.3a,b,d), in conjunction with (1.4.3) and (1.4.4), that the Stokes Δ will in general be larger than the antiStokes Δ and that the antiStokes P_c will be larger than the Stokes P_c. If the chiral distortion is sufficiently weak that the induced electric dipole contribution to the $j_e \leftarrow n_e$ transition moment is much smaller than the fully allowed magnetic dipole contribution, the antiStokes Δ and Stokes P_c might not be observed at all. Such asymmetry would be less at transparent frequencies because many excited electronic states can then contribute. In 0° and 180° scattering the corresponding relationships are not as clear-cut because $(\tilde{G}_{\alpha\beta})_{mn}$ and $(\tilde{\mathcal{G}}_{\alpha\beta})_{mn}$ both contribute to Δ and P_c.

The situation for a vibrational resonance Raman process is more complicated. In a completely asymmetric (C_1) chiral molecule, all modes of vibration are formally totally symmetric so that the first term of (1.3.3), corresponding to no vibronic coupling, should contribute to the Stokes and antiStokes ROA observables in equal measure. However, certain vibronic coupling mechanisms might generate much larger contributions, so significant Stokes-antiStokes asymmetry could arise from the other terms in (1.3.3). If the resonance transition $j_e \leftarrow n_e$ is strongly magnetic dipole allowed but only weakly electric dipole allowed, it can be seen from (1.3.3), (1.2.3), (1.4.3) and (1.4.4) that in 90° scattering, the 0-0 Stokes Δ will be generally larger than the 0-1 Stokes Δ, and that the 1-0 antiStokes Δ will be larger than the 1-1 antiStokes Δ. Conversely for P_c. (Notice that the antiStokes 1-0 pathway is the "reverse" of the Stokes 0-0 pathway, and the antiStokes 1-1 is the "reverse" of the Stokes 0-1, so in this case the Stokes 0-0 Δ equals the antiStokes 1-0 P_c, and the Stokes 0-1 Δ equals the antiStokes 1-1 P_c). The opposite conclusions obtain if the resonance transition $j_e \leftarrow n_e$ is strongly electric dipole allowed but only weakly magnetic dipole allowed.

These results have important implications for natural resonance ROA studies of stereochemistry in biological molecules. Most effects would originate in vibrational Raman transitions, a good example being the porphyrin group (in which the 0-0 and 0-1 vibronic absorption bands are usually well-resolved) in different chiral environents in various haem proteins. But one should also keep a lookout for low-frequency electronic transitions, which are of great potential interest (haemocyanin provides a good example (Larrabe and Spiro, 1980) . In such studies, a single Stokes Δ or P_c spectrum at one resonance frequency could be quite misleading: little or no effects might be observed, whereas large effects might result at a different excitation frequency or in the antiStokes spectrum. Since antiStokes ROA is unlikely to be observable beyond a few hundred cm^{-1} (Barron, 1976b), the best strategy would be to measure both Δ and P_c in the Stokes spectrum. Because all ROA instrumentation reported to date can only measure Δ , an improvement would be required to obtain P_c as well.

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2 INFLUENCE OF THE FINITE COLLECTION OPTIC ON ROA MEASUREMENTS

The equations of CID in ROA have been designed in the assumption of scattering at right angles, forward and backward. Here they will be extended to any direction. The collection optic, that is, the solid angle of the scattering source is taken into account. We shall define a new experimental dimensionless parameter in terms of power instead of intensity. Particular cases are derived. The influence of artifacts is also included in this discussion.

2.1 Polarized light.

In general, a polarized wave is that in which the plane of vibration follows certain characteristics. In an electromagnetic wave the plane of vibration contains the electric field vector $\underset{\sim}{E}$ and the propagation vector $\underset{\sim}{k}$ in the direction of the motion of the wave. If this plane is fixed it is said to be plane-polarized. Two monochromatic waves travelling in the same direction will interfere giving a polarized wave. The state of polarization of the interference will depend on the relative phase and magnitude of the propagating vectors.

In a right-handed space fixed coordinate system x, y, z (associated with unit vectors $\underset{\sim}{i}$, $\underset{\sim}{j}$, $\underset{\sim}{k}$) a plane wave light beam is described by eqs. (1.1.4a,b). At the same time, this wave can be considered as a sum of two coherent waves linearly polarized along x and y,

$$\tilde{\underset{\sim}{E}} = \tilde{E}_x \underset{\sim}{i} + \tilde{E}_y \underset{\sim}{j} . \qquad (2.1.1)$$

As it is said above the polarization of $\tilde{\underset{\sim}{E}}$ is determined by the relative phases and magnitudes of $\tilde{E}_x$ and $\tilde{E}_y$, if both have the same phase the polarization is linear, if the difference of phase is 90° the polarization is, in general, elliptical. We shall speak about right (or left) circular polarization when the plane of polarization has a clockwise or anticlockwise rotation viewed by an observer receiving the wave. Then we can write

$$\underset{\sim}{\tilde{E}}_{R,L} = \frac{1}{\sqrt{2}} E^{(0)} \left(\underset{\sim}{i} + e^{\mp i\pi/2} \underset{\sim}{j} \right) e^{-i\omega(t-z/c)}$$

$$= \frac{1}{\sqrt{2}} E^{(0)} \left(\underset{\sim}{i} \mp i \underset{\sim}{j} \right) e^{-i\omega(t-z/c)} . \qquad (2.1.2)$$

We see that the sign of $i\underset{\sim}{j}$ in (2.1.2) is determined by the arbitrary choice of sign in the exponent of (1.1.4a).

A general pure polarized light beam can be determined by three properties: its intensity, which is the time-averaged Poynting vector; the azimuth θ, which is the angle between the major axis of the polarization ellipse and the x-axis; and the ellipticity η of the polarization ellipse, which is defined as tg η = b/a where a and b are the major and minor axes (fig. 2.1). So we have $\eta = +45°$ for right circular polarization, $\eta = -45°$ for left circular polarization and $\eta = 0$ for linear polarization.

The three quantities I, θ and η can be extracted from the Stokes parameters,

$$S_0 = \tilde{E}_x \tilde{E}_x^* + \tilde{E}_y \tilde{E}_y^* = E^{(0)2} = 2\mu_0 c I , \qquad (2.1.3a)$$

$$S_1 = \tilde{E}_x \tilde{E}_x^* - \tilde{E}_y \tilde{E}_y^* = E^{(0)2} \cos 2\eta \cos 2\theta , \qquad (2.1.3b)$$

$$S_2 = -(\tilde{E}_x \tilde{E}_y^* + \tilde{E}_y \tilde{E}_x^*) = E^{(0)2} \cos 2\eta \sin 2\theta , \qquad (2.1.3c)$$

$$S_3 = -i(\tilde{E}_x \tilde{E}_y^* - \tilde{E}_y \tilde{E}_x^*) = E^{(0)2} \sin 2\eta . \qquad (2.1.3d)$$

This notation follows that of Born and Wolf (1981) but the sign convention differs from our definition of a positive azimuth, which leads to a minus sign in S_2 in (2.1.3c). S_0 is a measure of the total intensity, S_1 gives the difference in intensity transmitted by analysers that accept linear polarization with azimuth of 0 and 90°, S_2 has the same interpretation but with respect to the azimuths 45° and -45°, S_3 is the excess in intensity transmitted by a device that accepts right circularly polarized light over that transmitted by a device that accepts left.

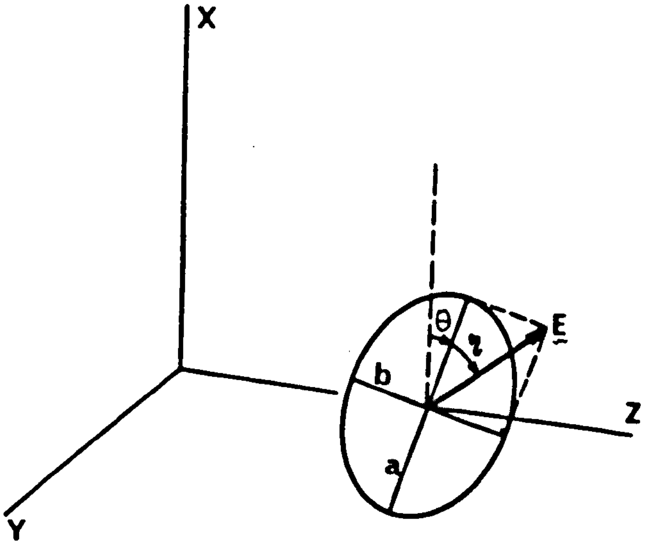


Figure 2.1.- The polarization ellipse referred to space fixed axes x,y and z.

Strictly speaking monochromatic light is always completely polarized. In practice we usually work with approximately monochromatic light, containing frequencies in a small interval centered on an apparent monochromatic frequency. Such waves are called quasi-monochromatic and can be represented by a superposition of pure monochromatic waves with various frequencies. So a quasi-monochromatic light beam will be partially polarized. The partial polarization can be introduced into this formalism by the definition of the degree of polarization, P, which takes values between 0 , for unpolarized light, and 1, for pure polarized light. The Stokes parameters are now,

$$S_0 = E^{(0)^2}, \tag{2.1.4a}$$

$$S_1 = P\, E^{(0)^2} \cos 2\eta \cos 2\theta , \tag{2.1.4b}$$

$$S_2 = P\, E^{(0)^2} \cos 2\eta \sin 2\theta , \tag{2.1.4c}$$

$$S_3 = P\, E^{(0)^2} \sin 2\eta . \tag{2.1.4d}$$

and

$$P = (S_1^2 + S_2^2 + S_3^2)^{1/2} / S_0 . \tag{2.1.4e}$$

Then P is the ratio of the intensity of the polarized part of the beam to the total intensity. Thus a partially polarized beam can be decomposed into a polarized and unpolarized part. In this way we can consider that the Stokes parameters are the sums of the Stokes parameters of the polarized and unpolarized components.

2.2 Molecular scattering of polarized light in a general direction.

We shall use the Stokes parameter formalism to calculate all possible polarization effects in light scattering processes that involve interference between the forward-scattered and unscattered components. The Rayleigh and Raman scattering in any non-forward direction are included, and also Raman scattering in the forward direction, since interference with the unscattered wave does not occur on account of the different frequencies. Fig. 2.2 shows a molecule at the origin O of a right-handed space-fixed coordinate system x, y, z.

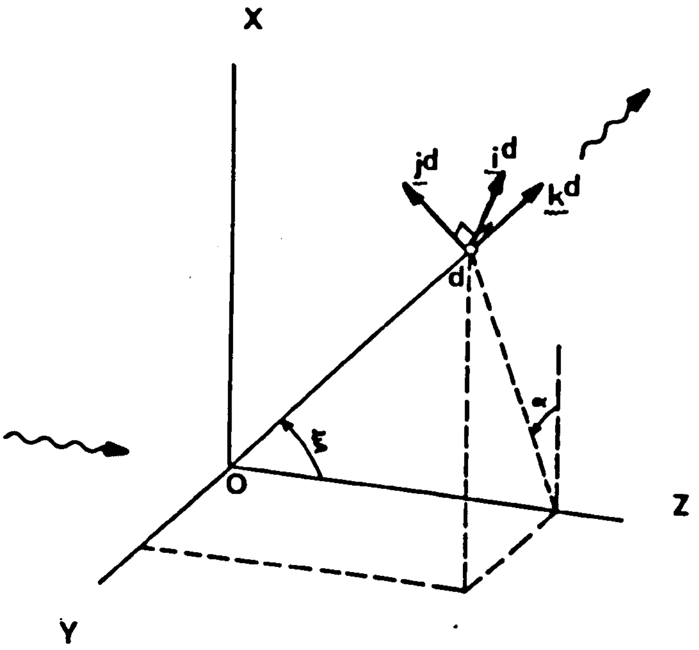


Figure 2.2.- Scattering geometry, where ξ is the scattering angle and α the azimuth.

An incident quasi-monochromatic light beam is propagating along the chosen vector $\underset{\sim}{\mathbf{k}}$, and is scattered in a direction given by the scattering angle ξ and azimuth α. The space-fixed coordinates are chosen so that the scattering direction corresponds to the vector $\underset{\sim}{\mathbf{k}}^d$ and the scattering plane is formed by $\underset{\sim}{\mathbf{j}}^d$ and $\underset{\sim}{\mathbf{k}}^d$. A coordinate system x^d, y^d, z^d (associated with unit vectors $\underset{\sim}{\mathbf{i}}^d$, $\underset{\sim}{\mathbf{j}}^d$, $\underset{\sim}{\mathbf{k}}^d$) is assigned to the scattering beam propagating along $\underset{\sim}{\mathbf{k}}^d$. From fig. (2.2) the two sets of unit vectors are related by,

$$\underset{\sim}{i}^d = \sin\alpha\,\underset{\sim}{i} - \cos\alpha\,\underset{\sim}{j}\,, \tag{2.2.1a}$$

$$\underset{\sim}{j}^d = \cos\xi\cos\alpha\,\underset{\sim}{i} + \cos\xi\sin\alpha\,\underset{\sim}{j} - \sin\xi\,\underset{\sim}{k}\,, \tag{2.2.1b}$$

$$\underset{\sim}{k}^d = \sin\xi\cos\alpha\,\underset{\sim}{i} + \sin\xi\sin\alpha\,\underset{\sim}{j} + \cos\xi\,\underset{\sim}{k}\,. \tag{2.2.1c}$$

The Stokes parameters of the scattered electric vector $\underset{\sim}{\tilde{\mathbf{E}}}^d$ in the x^d, y^d, z^d system are:

$$S_0^d = \tilde{E}^d_{x^d}\tilde{E}^{d*}_{x^d} + \tilde{E}^d_{y^d}\tilde{E}^{d*}_{y^d}\,, \tag{2.2.2a}$$

$$S_1^d = \tilde{E}^d_{x^d}\tilde{E}^{d*}_{x^d} - \tilde{E}^d_{y^d}\tilde{E}^{d*}_{y^d}\,, \tag{2.2.2b}$$

$$S_2^d = -(\tilde{E}^d_{x^d}\tilde{E}^{d*}_{y^d} + \tilde{E}^d_{y^d}\tilde{E}^{d*}_{x^d}), \tag{2.2.2c}$$

$$S_3^d = -i(\tilde{E}^d_{x^d}\tilde{E}^{d*}_{y^d} - \tilde{E}^d_{y^d}\tilde{E}^{d*}_{x^d}). \tag{2.2.2d}$$

Considering $\tilde{E}^{d}_{x}d$ and $\tilde{E}^{d}_{y}d$ with respect to the system of axes attached to the molecule we get

$$\tilde{E}^d_{x^d} = \sin\alpha\,\tilde{E}^d_x - \cos\alpha\,\tilde{E}^d_y\,, \tag{2.2.3a}$$

$$\tilde{E}^d_{y^d} = \cos\xi\cos\alpha\,\tilde{E}^d_x + \cos\xi\sin\alpha\,\tilde{E}^d_y - \sin\xi\,\tilde{E}^d_z\,. \tag{2.2.3b}$$

So, the Stokes parameters become

$$S_0 = (\sin^2\alpha + \cos^2\alpha\cos^2\xi)\,\tilde{E}^d_x\tilde{E}^{d*}_x + (\cos^2\alpha + \sin^2\alpha\cos^2\xi)\,\tilde{E}^d_y\tilde{E}^{d*}_y$$
$$+ \sin^2\xi\,\tilde{E}^d_z\tilde{E}^{d*}_z - \sin\alpha\cos\alpha\sin^2\xi\,(\tilde{E}^d_x\tilde{E}^{d*}_y + \tilde{E}^d_y\tilde{E}^{d*}_x)$$
$$- [(\tilde{E}^d_x\tilde{E}^{d*}_z + \tilde{E}^d_z\tilde{E}^{d*}_x)\cos\alpha + (\tilde{E}^d_y\tilde{E}^{d*}_z + \tilde{E}^d_z\tilde{E}^{d*}_y)\sin\alpha]\cos\xi\sin\xi\,, \tag{2.2.4a}$$

$$S_1 = (\sin^2\alpha - \cos^2\alpha\cos^2\xi)\,\tilde{E}^d_x\tilde{E}^{d*}_x + (\cos^2\alpha - \sin^2\alpha\cos^2\xi)\,\tilde{E}^d_y\tilde{E}^{d*}_y$$
$$- \sin^2\xi\,\tilde{E}^d_z\tilde{E}^{d*}_z - (1+\cos^2\xi)\sin\alpha\cos\alpha\,(\tilde{E}^d_x\tilde{E}^{d*}_y + \tilde{E}^d_y\tilde{E}^{d*}_x)$$
$$+ [(\tilde{E}^d_y\tilde{E}^{d*}_z + \tilde{E}^d_z\tilde{E}^{d*}_y)\sin\alpha + (\tilde{E}^d_x\tilde{E}^{d*}_z + \tilde{E}^d_z\tilde{E}^{d*}_x)\cos\alpha]\sin\xi\cos\xi\,, \tag{2.2.4b}$$

$$S_2 = -2(\tilde{E}^d_x\tilde{E}^{d*}_x + \tilde{E}^d_y\tilde{E}^{d*}_y)\sin\alpha\cos\alpha\cos\xi$$
$$+ (\tilde{E}^d_x\tilde{E}^{d*}_y + \tilde{E}^d_y\tilde{E}^{d*}_x)(\cos^2\alpha - \sin^2\alpha)\cos\xi + [(\tilde{E}^d_z\tilde{E}^{d*}_x + \tilde{E}^d_x\tilde{E}^{d*}_z)\sin\alpha$$
$$- (\tilde{E}^d_y\tilde{E}^{d*}_z + \tilde{E}^d_z\tilde{E}^{d*}_y)\cos\alpha]\sin\xi\,, \tag{2.2.4c}$$

$$S_3 = -i\{(\tilde{E}^d_x\tilde{E}^{d*}_y - \tilde{E}^d_y\tilde{E}^{d*}_x)\cos\xi + [-(\tilde{E}^d_x\tilde{E}^{d*}_z - \tilde{E}^d_z\tilde{E}^{d*}_x)\sin\alpha$$
$$+ (\tilde{E}^d_y\tilde{E}^{d*}_z - \tilde{E}^d_z\tilde{E}^{d*}_y)\cos\alpha]\sin\xi\}. \tag{2.2.4d}$$

From (1.1.7) the products of the electric vectors of the scattered waves in terms of the scattering tensor and the electric vector of the incident wave is

$$\tilde{E}^d_\alpha\tilde{E}^{d*}_\beta = \left(\frac{\omega^2\mu_0}{4\pi R}\right)^2 \tilde{a}_{\alpha\gamma}\,\tilde{a}^*_{\beta\delta}\,\tilde{E}^{(0)}_\gamma\tilde{E}^{(0)*}_\delta\,. \tag{2.2.5}$$

Then, Stokes parameters(2.2.4a-d) of the scattered radiation as a function of the scattering tensor and the Stokes parameters of the incident wave are:

$$\begin{aligned}
S_0^d = \frac{N}{2}\Big\{&[(|\tilde{a}_{xx}|^2+|\tilde{a}_{xy}|^2)S_0+(|\tilde{a}_{xx}|^2-|\tilde{a}_{xy}|^2)S_1-2\,\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{xy})S_2-2\,\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{xy})S_3]\\
&\times(\sin^2\alpha+\cos^2\alpha\cos^2\xi)+[(|\tilde{a}_{yx}|^2+|\tilde{a}_{yy}|^2)S_0+(|\tilde{a}_{yx}|^2-|\tilde{a}_{yy}|^2)S_1-2\,\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{yy})S_2\\
&-2\,\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{yy})S_3](\cos^2\alpha+\sin^2\alpha\cos^2\xi)+[(|\tilde{a}_{zx}|^2+|\tilde{a}_{zy}|^2)S_0+(|\tilde{a}_{zx}|^2-|\tilde{a}_{zy}|^2)S_1\\
&-2\,\mathrm{Re}(\tilde{a}_{zx}\tilde{a}^*_{zy})S_2-2\,\mathrm{Im}(\tilde{a}_{zx}\tilde{a}^*_{zy})S_3]\sin^2\xi-[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}+\tilde{a}_{xy}\tilde{a}^*_{yy})S_0+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}\\
&-\tilde{a}_{xy}\tilde{a}^*_{yy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_2-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_3]\sin 2\alpha\sin^2\xi\\
&-[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}+\tilde{a}_{xy}\tilde{a}^*_{zy})S_0+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}-\tilde{a}_{xy}\tilde{a}^*_{zy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_2\\
&-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_3]\cos\alpha\sin 2\xi-[\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}+\tilde{a}_{yy}\tilde{a}^*_{zy})S_0+\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}\\
&-\tilde{a}_{yy}\tilde{a}^*_{zy})S_1-\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_2-\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_3]\sin\alpha\sin 2\xi\Big\},
\end{aligned}$$

(2.2.6a)

$$\begin{aligned}
S_1^d = \frac{N}{2}\Big\{&[(|\tilde{a}_{xx}|^2+|\tilde{a}_{xy}|^2)S_0+(|\tilde{a}_{xx}|^2-|\tilde{a}_{xy}|^2)S_1-2\,\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{xy})S_2-2\,\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{xy})S_3]\\
&\times(\sin^2\alpha-\cos^2\alpha\cos^2\xi)+[(|\tilde{a}_{yx}|^2+|\tilde{a}_{yy}|^2)S_0+(|\tilde{a}_{yx}|^2-|\tilde{a}_{yy}|^2)S_1-2\,\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{yy})S_2\\
&-2\,\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{yy})S_3](\cos^2\alpha-\sin^2\alpha\cos^2\xi)-[(|\tilde{a}_{zx}|^2+|\tilde{a}_{zy}|^2)S_0+(|\tilde{a}_{zx}|^2-|\tilde{a}_{zy}|^2)S_1\\
&-2\,\mathrm{Re}(\tilde{a}_{zx}\tilde{a}^*_{zy})S_2-2\,\mathrm{Im}(\tilde{a}_{zx}\tilde{a}^*_{zy})S_3]\sin^2\xi-[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}+\tilde{a}_{xy}\tilde{a}^*_{yy})S_0+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}\\
&-\tilde{a}_{xy}\tilde{a}^*_{yy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_2-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_3](1+\cos^2\xi)\sin 2\alpha\\
&+[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}+\tilde{a}_{xy}\tilde{a}^*_{zy})S_0+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}-\tilde{a}_{xy}\tilde{a}^*_{zy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_2\\
&-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_3]\cos\alpha\sin 2\xi+[\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}+\tilde{a}_{yy}\tilde{a}^*_{zy})S_0+\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}\\
&-\tilde{a}_{yy}\tilde{a}^*_{zy})S_1-\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_2-\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})]\sin\alpha\sin 2\xi\Big\},
\end{aligned}$$

(2.2.6b)

$$\begin{aligned}
S_2^d = N\Big\{&-\frac{1}{2}[(|\tilde{a}_{xx}|^2+|\tilde{a}_{xy}|^2+|\tilde{a}_{yx}|^2+|\tilde{a}_{yy}|^2)S_0+(|\tilde{a}_{xx}|^2-|\tilde{a}_{xy}|^2+|\tilde{a}_{yx}|^2-|\tilde{a}_{yy}|^2)S_1\\
&-2\,\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{xy}+\tilde{a}_{yx}\tilde{a}^*_{yy})S_2-2\,\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{xy}+\tilde{a}_{yx}\tilde{a}^*_{yy})]\cos\xi\sin 2\alpha\\
&+[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}+\tilde{a}_{xy}\tilde{a}^*_{yy})S_0+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yx}-\tilde{a}_{xy}\tilde{a}^*_{yy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_2\\
&-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{yy}+\tilde{a}_{yx}\tilde{a}^*_{xy})S_3]\cos 2\alpha\cos\xi+[\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}+\tilde{a}_{xy}\tilde{a}^*_{zy})S_0\\
&+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zx}-\tilde{a}_{xy}\tilde{a}^*_{zy})S_1-\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_2-\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_3]\\
&\times\sin\alpha\sin\xi-[\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}+\tilde{a}_{yy}\tilde{a}^*_{zy})S_0+\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zx}-\tilde{a}_{yy}\tilde{a}^*_{zy})S_1\\
&-\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_2-\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{zy}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_3]\cos\alpha\sin\xi\Big\},
\end{aligned}$$

(2.2.6c)

$$\begin{aligned}
S_3^d = N\Big\{&\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{yx}+\tilde{a}_{xy}\tilde{a}^*_{yy})S_0+\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{yx}-\tilde{a}_{xy}\tilde{a}^*_{yy})S_1+\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{xx}-\tilde{a}_{xy}\tilde{a}^*_{yx})S_2\\
&+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{yy}-\tilde{a}_{yx}\tilde{a}^*_{xy})S_3]\cos\xi-[\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{zx}+\tilde{a}_{xy}\tilde{a}^*_{zy})S_0+\mathrm{Im}(\tilde{a}_{xx}\tilde{a}^*_{zx}-\tilde{a}_{xy}\tilde{a}^*_{zy})S_1\\
&+\mathrm{Im}(\tilde{a}_{zy}\tilde{a}^*_{xx}+\tilde{a}_{zx}\tilde{a}^*_{xy})S_2+\mathrm{Re}(\tilde{a}_{xx}\tilde{a}^*_{zy}-\tilde{a}_{zx}\tilde{a}^*_{xy})S_3]\sin\alpha\sin\xi\\
&+[\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{zx}+\tilde{a}_{yy}\tilde{a}^*_{zy})S_0+\mathrm{Im}(\tilde{a}_{yx}\tilde{a}^*_{zx}-\tilde{a}_{yy}\tilde{a}^*_{zy})S_1+\mathrm{Im}(\tilde{a}_{zy}\tilde{a}^*_{yx}+\tilde{a}_{zx}\tilde{a}^*_{yy})S_2\\
&+\mathrm{Re}(\tilde{a}_{yx}\tilde{a}^*_{zy}-\tilde{a}_{zx}\tilde{a}^*_{yy})S_3]\cos\alpha\sin\xi\Big\}.
\end{aligned}$$

(2.2.6d)

(where $N = [(\omega^2\mu_0)/(4\pi R)]^2$).

The eqs. (2.2.6a,d) give the intensity and state of polarization of the scattered light for any direction coming from an incident beam of arbitrary polarization. The dispersive medium can be liquid or solid, transparent or absorbing, oriented or isotropic. We shall consider just the case of scattering from a transparent liquid in which the molecules are randomly oriented.

We can calculate the Stokes parameters for the most usual scattering geometries: forward, right angle and backward directions. These Stokes parameters are completely general for transparent or resonant frequencies, Rayleigh or Raman scattering. We shall write $(\tilde{\alpha}_{\alpha\beta})_{mn}$ as $\tilde{\alpha}_{\alpha\beta}$, etc. for brevity, and $K = (1/30)E_o^2N$.

a) Forward scattering,

$$S_0^d(0^\circ) = K\{6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta} \;-(2/c)\mathrm{Im}[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\beta\alpha}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}$$
$$- \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta}) - 6\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} + 5\tilde{\alpha}_{\alpha\alpha}\tilde{g}^*_{\beta\beta} - 5\tilde{\alpha}_{\alpha\beta}\tilde{g}^*_{\beta\alpha}]P\sin 2\eta\},$$

(2.2.7a

$$S_1^d(0^\circ) = K\{(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\cos 2\theta\cos 2\eta \;-(2/c)\mathrm{Re}[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}$$
$$+ \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta}) + 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} - 2\tilde{\alpha}_{\alpha\beta}\tilde{g}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}g^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{g}^*_{\beta\beta}]$$
$$\times P\cos 2\eta\sin 2\theta\},$$

(2.2.7b

$$S_3^d(0^\circ) = K\{(2/c)\mathrm{Im}[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(-2\tilde{\alpha}_{\alpha\beta}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) + 5\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} - 6\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha}$$
$$- 6\tilde{\alpha}_{\alpha\beta}\tilde{g}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}g^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}g^*_{\beta\beta}] + 5\,\mathrm{Im}(\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\cos 2\eta\sin 2\theta$$
$$+ 5\,\mathrm{Re}(-\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\sin 2\eta\}.$$

(2.2.7c

$$S_2^d(0^\circ) = K\{(2/c)\mathrm{Re}[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(-\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) - 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta}$$
$$+ 2\tilde{\alpha}_{\alpha\beta}\tilde{g}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{g}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}g^*_{\beta\beta}]P\cos 2\eta\cos 2\theta \;-\mathrm{Re}(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\beta}\tilde{a}^*_{\beta\alpha}$$
$$+ 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\cos 2\eta\sin 2\theta \;-\mathrm{Im}(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}_{\beta\beta})P\sin 2\eta\},$$

(2.2.7d

b) Right angle scattering,

$$\begin{aligned} S_0^d(90^\circ) = (1/2)K\Big[&(14\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta}) + (-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\cos 2\eta\cos 2\theta \\ &-(2/c)\mathrm{Re}\,(i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta})P\cos 2\eta\sin 2\theta \\ &-(2/c)\mathrm{Im}\,(i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} - 14\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta})P\sin 2\eta\Big], \end{aligned}$$

(2.2.8a)

$$\begin{aligned} S_1^d(90^\circ) = (1/2)K\Big[&(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})(1 + P\cos 2\eta\cos 2\theta) \\ &-(2/c)\mathrm{Re}\,(i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta})P\cos 2\eta\sin 2\theta \\ &-(2/c)\mathrm{Im}\,(-i\omega\ \varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\alpha\beta}\tilde{G}'_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta})P\sin 2\eta\Big], \end{aligned}$$

(2.2.8b)

$$\begin{aligned} S_2^d(90^\circ) = (K/c)\Big[&\mathrm{Re}\,(i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} - 2\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta}) \\ &+ \mathrm{Re}\,(i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\gamma\delta\beta} - 2\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta})P\cos 2\eta\cos 2\theta\Big], \end{aligned}$$

(2.2.8c)

$$\begin{aligned} S_3^d(90^\circ) = -(K/c)\Big[&\mathrm{Im}\,(-i(\omega/3)\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} + 14\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\alpha\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} - \tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta}) \\ &+ \mathrm{Im}\,(-i\omega\,\varepsilon_{\alpha\gamma\delta}\,\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} - 2\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta})P\cos 2\eta\cos 2\theta\Big]. \end{aligned}$$

(2.2.8d)

c) Backward scattering,

$$\begin{aligned} S_0^d(180^\circ) = K\Big\{&6\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta} + (2/c)\mathrm{Im}\,[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} + 2\tilde{\alpha}_{\beta\alpha}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta}) \\ &+ 6\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + \tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} - 5\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} + 5\tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta}]P\sin 2\eta\Big\}, \end{aligned}$$

(2.2.9a)

$$\begin{aligned} S_1^d(180^\circ) = K\Big\{&(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})P\cos 2\eta\cos 2\theta - (2/c)\mathrm{Re}\,[i(\omega/3)\varepsilon_{\alpha\gamma\delta}(-\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta} \\ &+ \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta}) + 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta} + 2\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\alpha\beta} - 3\tilde{\alpha}_{\alpha\beta}\tilde{\mathfrak{g}}^*_{\beta\alpha} - 3\tilde{\alpha}_{\alpha\alpha}\tilde{\mathfrak{g}}^*_{\beta\beta}] \\ &\times P\cos 2\eta\sin 2\theta\Big\}, \end{aligned}$$

(2.2.9b)

$$S_2^d(180^\circ) = K\{(2/c)\,\mathrm{Re}\,[\,i(\omega/3)\,\varepsilon_{\alpha\gamma\delta}(-\tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) - 2\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{G}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{G}^*_{\beta\beta}$$
$$- 2\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\mathcal{G}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\mathcal{G}^*_{\beta\beta}\,]\,P\cos 2\eta\cos 2\theta - \mathrm{Re}\,(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha}$$
$$+ 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})\,P\cos 2\eta\sin 2\theta - \mathrm{Im}\,(-2\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\alpha\beta} + 3\tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha} + 3\tilde{\alpha}_{\alpha\alpha}\tilde{\alpha}^*_{\beta\beta})\,P\sin 2\eta\,\}, \qquad (2.2.9c)$$

$$S_3^d(180^\circ) = -K\{(2/c)\,\mathrm{Im}\,[\,i(\omega/3)\,\varepsilon_{\alpha\gamma\delta}(-2\tilde{\alpha}_{\alpha\beta}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\beta\alpha}\tilde{A}^*_{\gamma\delta\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{A}}^*_{\gamma\delta\beta}) - 5\tilde{\alpha}_{\alpha\beta}\hat{G}^*_{\beta\alpha} + 5\hat{\alpha}_{\alpha\alpha}\hat{G}^*_{\beta\beta}$$
$$+ 6\tilde{\alpha}_{\alpha\beta}\tilde{\mathcal{G}}^*_{\alpha\beta} + \tilde{\alpha}_{\alpha\beta}\hat{\mathcal{G}}^*_{\beta\alpha} + \hat{\alpha}_{\alpha\alpha}\hat{\mathcal{G}}^*_{\beta\beta}\,] + 5\,\mathrm{Im}\,(-\tilde{\alpha}_{\alpha\alpha}\hat{\alpha}^*_{\beta\beta} + \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha})\,P\cos 2\eta\sin 2\theta$$
$$+ 5\,\mathrm{Re}\,(\tilde{\alpha}_{\alpha\alpha}\hat{\alpha}^*_{\beta\beta} - \tilde{\alpha}_{\alpha\beta}\tilde{\alpha}^*_{\beta\alpha})\,P\sin 2\eta\,\}. \qquad (2.2.9d)$$

2.3 Natural Rayleigh and Raman optical activity.

Rayleigh and Raman scattering from optically active samples can show additional polarization effects that originate in the different response of an optically active molecule to right and left circularly polarized incident light. The mean contribution to this "opticaly active" scattering at transparent frequencies arises from interference between the Rayleigh (or Raman) waves generated by $\alpha_{\alpha\beta}$ (or$(\alpha_{\alpha\beta})_{m_v n_v}$) with $G'_{\alpha\beta}$ (or $(G'_{\alpha\beta})_{m_v n_v}$) and $A_{\alpha\beta\gamma}$ (or $(A_{\alpha\beta\gamma})_{m_v n_v}$). Terms involving interference between $\alpha'_{\alpha\beta}$ and $G_{\alpha\beta}$ plus $A'_{\alpha\beta\gamma}$ (or its corresponding vibrational transitions) are expected to be negligible (at least for molecules in non-degenerate electronic states) and are not included.

For scattered radiation in a direction given by the azimuth α and a scattering angle ξ, the CID $\Delta_a(\alpha,\xi)$ are given in the eqs. (2.3.15). The numerator is a measure of the CID and the denominator corresponds to the Raman spectrum. Our goal is to generalize the expression (2.3.15) to any direction in the space, and to include the contribution from optical artifacts, which is necessary in cases in which the incident light is not perfectly right and left circularly polarized.

From the Stokes parameters (2.1.4a,d) we see that for pure right (left) circularly polarized light we have: $S_o(1,0,0,1)$ and $S_o(1,0,0,-1)$ in each case; otherwise the Stokes parameters are $(S_o, S_1^R, S_2^R, S_3^R)$ and $(S_o, S_1^L, S_2^L, S_3^L)$. Let us consider a slight imperfection in the R and L circular polarization states which we characterize by a perturbation $\delta_{R,L}$ of the corresponding ellipticity $\pm 45^o$:

$$\eta_R = 45^\circ + \delta_R \simeq 45^\circ + \delta \,, \qquad (2.3.1a)$$

$$\eta_L = -45^\circ + \delta_L \simeq -45^\circ + \delta \,, \qquad (2.3.1b)$$

Then the perturbation is the same in both cases ($\delta_R = \delta_L = \delta$). Within this assumption, the degree of polarization P is the same in both cases so,

$$S_1^R - S_1^L = 4 S_0 P \delta \cos(\theta_R + \theta_L) \cos(\theta_R - \theta_L) \,, \qquad (2.3.2a)$$

$$S_2^R - S_2^L = -4 S_0 P \delta \sin(\theta_R + \theta_L) \cos(\theta_R - \theta_L) \,, \qquad (2.3.2b)$$

$$S_3^R - S_3^L = 2 S_0 P \,, \qquad (2.3.2c)$$

and

$$S_1^R + S_1^L = 4 S_0 P \delta \sin(\theta_R + \theta_L) \sin(\theta_R - \theta_L) \,, \qquad (2.3.3a)$$

$$S_2^R + S_2^L = -4 S_0 P \delta \cos(\theta_R + \theta_L) \sin(\theta_R - \theta_L) \,, \qquad (2.3.3b)$$

$$S_3^R + S_3^L = 0 \,. \qquad (2.3.3c)$$

Where θ_R and θ_L refer to the azimuth of the small linearly polarized contaminants that are implied by the introduction of δ. We observe that for values of $\delta < 10^o$, $(S^R_{1,2} \pm S^L_{1,2})$ is three orders of magnitude less than $(S^R_3 - S^L_3)$. From now on we shall abreviate the notation $(\theta_R \pm \theta_L) = (\pm)$.

From fig.(2.2) x^d is the direction of the polarized scattered light (‖) and y^d that of the corresponding depolarized scattered light (⊥). Here (‖) and (⊥) refer to components parallel and perpendicular to the polarization plane. Then,

$$I^{\mathcal{P}}_{x^d} = \frac{1}{4}\left(\frac{\epsilon\epsilon_0}{\mu\mu_0}\right)^{1/2} \left(S^d_0 + S^d_1\right)^{\mathcal{P}} , \tag{2.3.4a}$$

$$I^{\mathcal{P}}_{y^d} = \frac{1}{4}\left(\frac{\epsilon\epsilon_0}{\mu\mu_0}\right)^{1/2} \left(S^d_0 - S^d_1\right)^{\mathcal{P}} , \qquad (\mathcal{P} = \mathrm{R\ or\ L}) \tag{2.3.4b}$$

$$I^{\mathcal{P}} = \frac{1}{2}\left(\frac{\epsilon\epsilon_0}{\mu\mu_0}\right)^{1/2} S^d_0 \ . \tag{2.3.4c}$$

I is the total intensity, $I = I_{\parallel} + I_{\perp}$. In these circumstances, if we do not consider terms three orders of magnitude less than the first one in (2.3.2-3a,c) we get

Total intensity:

$$\begin{aligned}
I^R - I^L = 2MP \Big\{ & [\![-(3\alpha_{\alpha\alpha}\alpha_{\beta\beta} + \alpha_{\alpha\beta}\alpha_{\alpha\beta})2\delta\cos(+)\cos(-) + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} \\
& + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\left(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\big]]\!] \\
& \times(\sin^2\alpha + \cos^2\alpha\cos^2\xi) + [\![(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\cos(+)\cos(-) \\
& + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\big(-5\alpha_{\alpha\beta}G'_{\alpha\beta} \\
& + 5\alpha_{\alpha\alpha}G'_{\beta\beta} - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\big)\big]]\!](\cos^2\alpha + \sin^2\alpha\cos^2\xi) \\
& + \frac{4}{c}\left[3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} - 2\cos\xi\left(\frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\right] \\
& \times\sin^2\xi - \left[2(3\alpha_{\alpha\alpha}\alpha_{\beta\beta} + \alpha_{\alpha\beta}\alpha_{\alpha\beta})2\delta\sin(+)\cos(-)\right]\sin 2\alpha\sin^2\xi \\
& + \frac{4}{c}\left(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)2\cos\xi\sin^2\xi\Big\} ,
\end{aligned} \tag{2.3.5a}$$

$$I^R + I^L = 2M\left[(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta})(1+\cos^2\xi) + 2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})\sin^2\xi\right] . \tag{2.3.5b}$$

Polarized intensity (i.e. transmitted through a vertical analyzer)

$$\begin{aligned} I^R_{xd} - I^L_{xd} = {} & MP\Big\{\Big[-(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\cos(+)\cos(-) + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} \\ & + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\,(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})\big]\Big] \\ & \times 2\sin^2\alpha + \Big\llbracket(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\cos(+)\cos(-) + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} \\ & + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\,(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})\big]\Big\rrbracket \\ & \times 2\cos^2\alpha + \big[-2(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\sin(+)\cos(-)\big]2\sin 2\alpha\Big\}, \end{aligned} \tag{2.3.6a}$$

$$I^R_{xd} + I^L_{xd} = 2M(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta})\ . \tag{2.3.6b}$$

Depolarized intensity (i.e. transmitted through a horizontal analizer)

$$\begin{aligned} I^R_{yd} - I^L_{yd} = {} & MP\Big\{\Big\llbracket-(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\cos(+)\cos(-) + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} \\ & + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\,(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})\big]\Big\rrbracket \\ & \times 2\cos^2\alpha\cos^2\xi + \Big\llbracket(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\cos(+)\cos(-) + \frac{2}{c}\big[7\alpha_{\alpha\beta}G'_{\alpha\beta} \\ & - \omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})\big]\Big\rrbracket 2\sin^2\alpha\cos^2\xi + \frac{4}{c}\big[3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} \\ & + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \cos\xi\,(-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} \\ & - \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} - 2\cos\xi\,(\frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})\big]2\sin^2\xi \\ & + \frac{1}{c}\big[-5\alpha_{\alpha\beta}G'_{\alpha\beta} + 5\alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})4\cos\xi\sin^2\xi \\ & + 2(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})2\delta\sin(+)\cos(-)\big]2\sin 2\alpha\cos^2\xi\Big\}, \end{aligned} \tag{2.3.7a}$$

$$I^R_{yd} + I^L_{yd} = 2M\big[(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta})\cos^2\xi + 2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})\sin^2\xi\big]. \tag{2.3.7b}$$

Where $M = (1/30)[(\epsilon\epsilon_0)/(\mu\mu_0)]^{1/2}NS_0$.

These equations contain the information on Rayleigh and Raman CID. At this point we are interested in the influence of artifacts and the angular dependence of the CID. In all cases the CID is affected by the degree of polarization P of the incident light . When $\delta = 0$, or $\theta_R = \theta_L = 45^\circ$, we have no optical artifacts, otherwise it can be noticed that the artifacts are of the same order of magnitude as the proper CID measure. Studies of artifacts have been carried out (Hug, 1979; Barron and Vrbancich, 1984) but never have the equations shown together the contributions of ROA and the artifacts. From these general cases, (2.3.5) to (2.3.7),we can write equations for scattering at right angle, and write, forward and backward direction:

1.- Forward scattering, $\xi = \alpha = 0^\circ$.

$$(I^R-I^L)(0^\circ,0^\circ) = 2MP\left[\frac{8}{c}\left(\alpha_{\alpha\beta}G'_{\alpha\beta} + 3\alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\right]. \quad (2.3.8a)$$

$$(I^R+I^L)(0^\circ,0^\circ) = 2M\left[2\left(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}\right)\right]. \quad (2.3.8b)$$

2.- Backward scattering, $\xi = 180^\circ$, $\alpha = 0^\circ$.

$$(I^R-I^L)(0^\circ,180^\circ) = 2MP\left[\frac{16}{c}\left(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\right]. \quad (2.3.9a)$$

$$(I^R+I^L)(0^\circ,180^\circ) = 2M\left[2\left(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}\right)\right]. \quad (2.3.9b)$$

3.- Scattering at right angles, $\xi = \alpha = 90^\circ$.

3.1.- Total intensity,

$$\begin{aligned}(I^R-I^L)(90^\circ,90^\circ) = 2MP\Big[&-\left(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta}\right)2\delta\cos(+)\cos(-)\\ &+ \frac{2}{c}\left(13\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\Big].\end{aligned} \quad (2.3.10a)$$

$$(I^R+I^L)(90^\circ,90^\circ) = 2M\left[2\left(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}\right)\right]. \quad (2.3.10b)$$

3.2.- Depolarized,

$$(I^R_{yd}-I^L_{yd})(90^\circ,90^\circ) = 2MP\left[\frac{4}{c}\left(\alpha_{\alpha\beta}G'_{\alpha\beta}-\alpha_{\alpha\alpha}G'_{\beta\beta}-\frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\right]. \tag{2.3.11a}$$

$$(I^R_{yd}+I^L_{yd})(90^\circ,90^\circ) = 2M\left[2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta}-\alpha_{\alpha\alpha}\alpha_{\beta\beta})\right]. \tag{2.3.11b}$$

3.3.- Polarized,

$$\begin{aligned}(I^R_{xd}-I^L_{xd})(90^\circ,90^\circ) = {} & 2MP\Big[-(\alpha_{\alpha\beta}\alpha_{\alpha\beta}+3\alpha_{\alpha\alpha}\alpha_{\beta\beta})\,2\delta\cos(+)\cos(-)\\ & +\frac{2}{c}\left(7\alpha_{\alpha\beta}G'_{\alpha\beta}+\alpha_{\alpha\alpha}G'_{\beta\beta}+\frac{\omega}{3}\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}\right)\Big].\end{aligned} \tag{2.3.12a}$$

$$(I^R_{xd}+I^L_{xd})(90^\circ,90^\circ) = 2M\left[(7\ \alpha_{\alpha\beta}\alpha_{\alpha\beta}+\alpha_{\alpha\alpha}\alpha_{\beta\beta})\right]. \tag{2.3.12b}$$

From (2.3.8.a) and (2.3.9.a) we realise that forward and backward directions are artifact-independent, as well as the depolarized direction at right angles. Thereby the polarized case, eq. (2.3.11a), is strongly affected by artifacts and experimental measurements must be made carefully in order to suppress them. Hug and Surbeck (1979) have discussed the experimental influences on ROA and we shall refer to them for further explanations.

In these equations we have not included the contribution to the artifacts from the antisymmetric polarizability, but this is straight forwardly incorporated by considering,

$$\begin{aligned}(\alpha_{\alpha\beta}\alpha_{\alpha\beta}+3\alpha_{\alpha\alpha}\alpha_{\beta\beta}) \rightarrow {} & (\alpha_{\alpha\beta}\alpha_{\alpha\beta}+3\alpha_{\alpha\alpha}\alpha_{\beta\beta})+(3\alpha'_{\alpha\alpha}\alpha'_{\beta\beta}-5\alpha'_{\alpha\beta}\alpha'_{\alpha\beta})\\ = {} & \left(\beta^2+\frac{5}{3}\beta'^2\right)\left(\frac{1}{\rho}-1\right).\end{aligned} \tag{2.3.13}$$

Here we have used the definitions (see for instance Barron, 1982) of the isotropic invariant α^2, the anisotropic invariant β^2, the anisotropic invariant associated with the antisymmetric polarizability β'^2, and the depolarization ratio ρ (for incident linear polarized light) like,

$$\alpha^2 = \frac{1}{9}\alpha_{\alpha\alpha}\alpha_{\beta\beta} \quad , \tag{2.3.14a}$$

$$\beta^2 = \frac{1}{2}\left(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}\right) , \tag{2.3.14b}$$

$$\beta'^2 = \frac{3}{2}\alpha'_{\alpha\beta}\alpha'_{\alpha\beta} \quad , \tag{2.3.14c}$$

$$\rho = (3\beta^2 + 5\beta'^2)/(45\alpha^2 + 4\beta^2) . \tag{2.3.14d}$$

The CIDs are the only experimental measurements in ROA carried out to date. For that reason, and for correlating posterior equations we shall write down explicitly their expressions at vibrational transparent frequencies in absence of artifacts (Barron and Buckingham, 1971)

$$\Delta(0^\circ) = \frac{4(3\alpha_{\alpha\alpha}G'_{\beta\beta} + \alpha_{\alpha\beta}G'_{\alpha\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha_{\lambda\mu} + \alpha_{\lambda\lambda}\alpha_{\mu\mu})} , \tag{2.3.15a}$$

$$\Delta(180^\circ) = \frac{8(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha_{\lambda\mu} + \alpha_{\lambda\lambda}\alpha_{\mu\mu})} , \tag{2.3.15b}$$

$$\Delta_x(90^\circ) = \frac{2(7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha_{\lambda\mu} + \alpha_{\lambda\lambda}\alpha_{\mu\mu})} , \tag{2.3.15c}$$

$$\Delta_z(90^\circ) = \frac{4(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\lambda\mu}\alpha_{\lambda\mu} - \alpha_{\lambda\lambda}\alpha_{\mu\mu})} . \tag{2.3.15d}$$

2.4 ROA in terms of power.

The spectrophotometer does not measure the intensity but the power. Will the equations of the CID-parameter, Δ, remain when the collection angle is taken into account? In principle we can think that the same factors are going to affect the numerator and denominator and both will cancel each other. This is not general for any solid angle but particularly right for the special case in which the solid angle is very small ($\Omega \rightarrow 0$). Nevertheless this is the most interesting at the time of the experiment, so the previous theory is saved. The aim of this work is to know the limits between which we are working.

By definition, the intensity is

$$I = \frac{1}{R^2} \frac{dW}{d\Omega} , \tag{2.4.1}$$

where W is the power collected at a distance R from the source through a solid angle Ω . If we use spherical coordinates $d\Omega = \sin\xi \, d\xi \, d\alpha$, then

$$W_a^{\varphi} = R^2 \int_{\xi}\int_{\alpha} I_a^{\varphi}(\alpha,\xi) \sin\xi \, d\xi \, d\alpha . \tag{2.4.2}$$

Now we will particularize our problem in order to know the limits of integration. It is possible to realize the importance of a good knowledge of the angular dependence of the intensity, because otherwise we could not resolve (2.4.2). The different cases correspond to what have been treated previously: scattering at right angles, forward and backward. See fig. (2.3a,c).

1.- Forward scattering,

$$W_a^{\varphi} = R^2 \int_{\xi=0}^{\Delta\xi/2} \int_{\alpha=0}^{2\pi} I_a^{\varphi}(0,0) \sin\xi \, d\xi \, d\alpha . \tag{2.4.3}$$

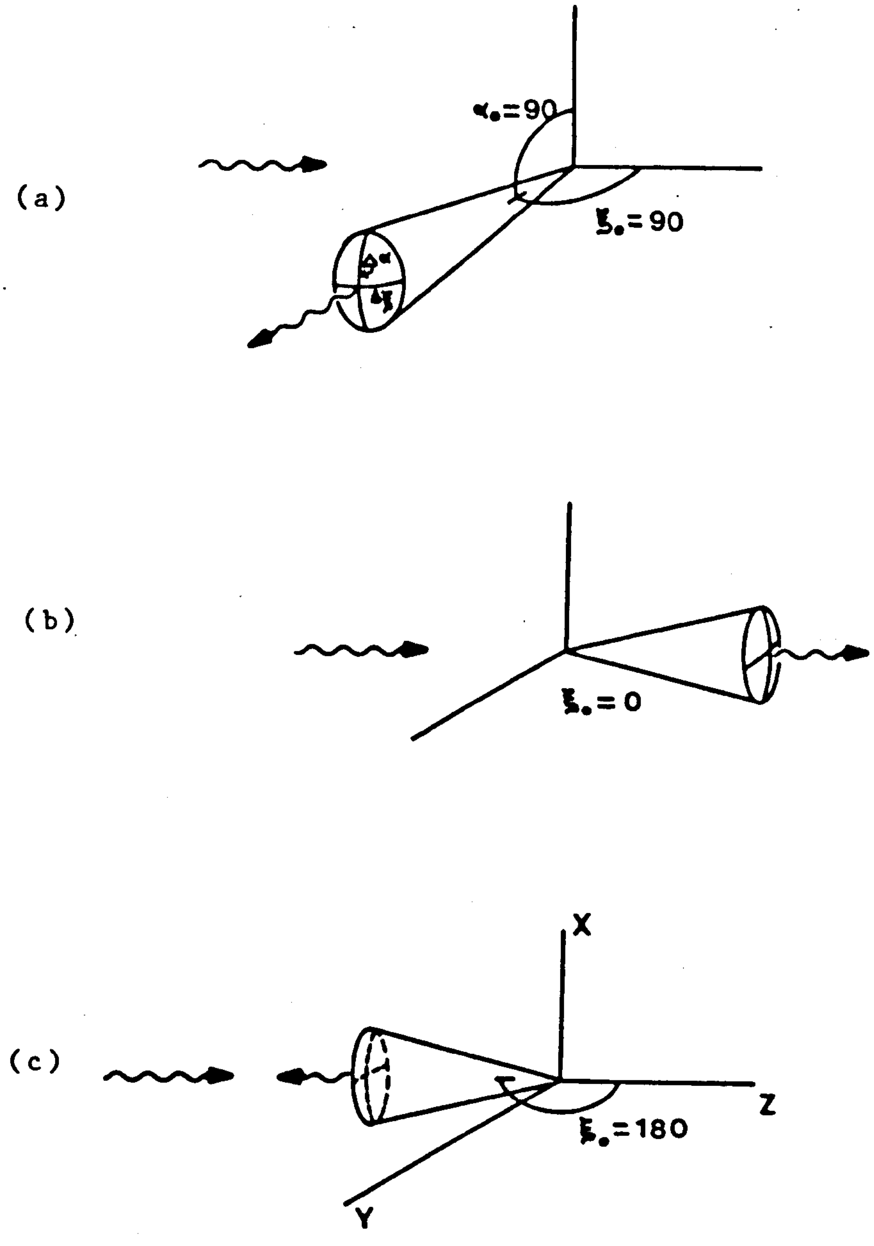


Figure 2.3.- Scattering into several directions:(a) right angles, (b) forward, (c) backward. $\Delta\xi$ and $\Delta\alpha$ depicted in the figure can be different or equal (circular lens).

2.- Backward scattering,

$$W_a^{\varphi} = R^2 \int_{\xi=\pi-\Delta\xi/2}^{\pi} \int_{\alpha=0}^{2\pi} I_a^{\varphi}(0,\pi) \sin\xi \, d\xi \, d\alpha . \qquad (2.4.4)$$

3.- Scattering at right angles,

$$W_a^{\varphi} = R^2 \int_{\xi=\frac{\pi}{4}-\frac{\Delta\xi}{2}}^{\frac{\pi}{4}+\frac{\Delta\xi}{2}} \int_{\alpha=\frac{\pi}{4}-\frac{\Delta\alpha}{2}}^{\frac{\pi}{4}+\frac{\Delta\alpha}{2}} I_a^{\varphi}\left(\frac{\pi}{2},\frac{\pi}{2}\right) \sin\xi \, d\xi \, d\alpha . \qquad (2.4.5)$$

Now we are able to calculate the terms $(W_a^R - W_a^L)$, that is the circular power difference (CPD). Using (2.4.3-5) and (2.3.8,13) we obtain,

1.- Forward scattering,

$$W^R - W^L = 4MPR^2 \left\{ \frac{2}{c} A \left[2\pi \sin^2\frac{\Delta\xi}{4} + \frac{\pi}{3}\left(1-\cos^3\frac{\Delta\xi}{2}\right)\right] + \frac{1}{c} B \left[\pi \sin^2\frac{\Delta\xi}{2} + \frac{\pi}{2}\left(1-\cos^4\frac{\Delta\xi}{2}\right)\right] + \frac{4\pi}{c} C \left(\frac{1}{3}\cos^3\frac{\Delta\xi}{2} - \cos\frac{\Delta\xi}{2} + \frac{2}{3}\right) + \frac{1}{c}(B-4D)\frac{\pi}{2}\sin^4\frac{\Delta\xi}{2} \right\} . \qquad (2.4.6)$$

2.- Backward scattering,

$$W^R - W^L = 4MPR^2 \left\{ \frac{2}{c} A \left[2\pi \sin^2\frac{\Delta\xi}{4} + \frac{\pi}{3}\left(1-\cos^3\frac{\Delta\xi}{2}\right)\right] - \frac{1}{c} B \left[\pi \sin^2\frac{\Delta\xi}{2} + \frac{\pi}{2}\left(1-\cos^4\frac{\Delta\xi}{2}\right)\right] + \frac{4\pi}{c} C \left(\frac{1}{3}\cos^3\frac{\Delta\xi}{2} - \cos\frac{\Delta\xi}{2} + \frac{2}{3}\right) - \frac{1}{c}(B-4D)\frac{\pi}{2}\sin^4\frac{\Delta\xi}{2} \right\} . \qquad (2.4.7)$$

3.- Scattering at right angles.

3.1- Depolarized,

$$W^R_{yd} - W^L_{yd} = 2MPR^2 \Big[\left(-E + \tfrac{1}{c} A\right) \tfrac{2}{3} \sin^3 \tfrac{\Delta\xi}{2} \left(\Delta\alpha - \sin\Delta\alpha\right)$$

$$+ \left(E + \tfrac{1}{c} A\right) \tfrac{2}{3} \sin^3 \tfrac{\Delta\xi}{2} \left(\Delta\alpha + \sin\Delta\alpha\right) + \tfrac{4}{c} C \, \Delta\alpha \left(2 \sin\tfrac{\Delta\xi}{2} - \tfrac{2}{3} \sin^3 \tfrac{\Delta\xi}{2}\right)\Big].$$

(2.4.8a)

3.2.- Polarized,

$$W^R_{xd} - W^L_{xd} = 2MPR^2 \Big[\left(-E + \tfrac{1}{c} A\right) 2 \sin\tfrac{\Delta\xi}{2} \left(\Delta\alpha + \sin\Delta\alpha\right) + \left(E + \tfrac{1}{c} A\right) 2 \sin\tfrac{\Delta\xi}{2} \left(\Delta\alpha - \sin\Delta\alpha\right)\Big].$$

(2.4.8b)

We have used the equations (2.3.14.a,d) in establishing the definitions of A - E as:

$$A = 7 \alpha_{\alpha\beta} G'_{\alpha\beta} + \alpha_{\alpha\alpha} G'_{\beta\beta} + \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta} , \qquad (2.4.9a)$$

$$B = -5 \alpha_{\alpha\beta} G'_{\alpha\beta} + 5 \alpha_{\alpha\alpha} G'_{\beta\beta} - \omega \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta} , \qquad (2.4.9b)$$

$$C = 3 \alpha_{\alpha\beta} G'_{\alpha\beta} - \alpha_{\alpha\alpha} G'_{\beta\beta} - \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta} , \qquad (2.4.9c)$$

$$D = \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta} , \qquad (2.4.9d)$$

$$E = 2 \left(\beta^2 + \frac{5}{3} \beta'^2\right)\left(\frac{1}{\rho} - 1\right) \delta \cos(+) \cos(-) . \qquad (2.4.9e)$$

Likewise it is possible to calculate the sums ($W^R_a + W^L_a$) in the different experiments,

1.- Forward scattering,

$$W^R + W^L = 2MPR^2 \Big\{ \left(7 \alpha_{\alpha\beta} \alpha_{\alpha\beta} + \alpha_{\alpha\alpha} \alpha_{\beta\beta}\right) \left[4\pi \sin^2 \tfrac{\Delta\xi}{4} + \tfrac{2\pi}{3} \left(1 - \cos^3 \tfrac{\Delta\xi}{2}\right)\right]$$

$$+ 2 \left(3 \alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}\right) 2\pi \left(\tfrac{1}{3} \cos^3 \tfrac{\Delta\xi}{2} - \cos\tfrac{\Delta\xi}{2} + \tfrac{2}{3}\right) \Big\} . \qquad (2.4.10)$$

2.- Backward scattering,

$$W^R + W^L = 2MPR^2 \Big\{ (7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}) \Big[4\pi \sin^3\frac{\Delta\xi}{4} + \frac{2\pi}{3}\Big(1 - \cos^3\frac{\Delta\xi}{2}\Big) \Big]$$

$$+ 2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})\, 2\pi \Big(\frac{1}{3}\cos^3\frac{\Delta\xi}{2} - \cos\frac{\Delta\xi}{2} + \frac{2}{3}\Big) \Big\} . \quad (2.4.11)$$

3.- Scattering at right angles.

3.1.- Depolarized,

$$W^R_{y^d} + W^L_{y^d} = 2MPR^2 \Big[(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}) \frac{2}{3} \Delta\alpha \sin^3\frac{\Delta\xi}{2} + 4(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})$$

$$\times \Delta\alpha \Big(\sin\frac{\Delta\xi}{2} - \frac{1}{3}\sin^3\frac{\Delta\xi}{2} \Big) \Big] . \quad (2.4.12a)$$

3.2.- Polarized,

$$W^R_{x^d} + W^L_{x^d} = 2MPR^2 \,(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta})\, 2\,\Delta\alpha \sin\frac{\Delta\xi}{2} . \quad (2.4.12b)$$

At this point we will introduce a dimensionless parameter ∇_a, analogous to Δ_a (1.3.1), but in terms of power instead of intensity.

$$\nabla_a = (W^R_a - W^L_a)/(W^R_a + W^L_a) . \quad (2.4.13)$$

This parameter includes the same information about the molecular multipole tensor as Δ_a, but in addition includes the experimental conditions on the finite collection optic cone. Observing the numerator (2.4.6-8) we deduce that extra contributions can be collected coming from products of the polarizability with the optical activity tensors. It is interesting to know what is the relationship between (2.3.15) and (2.4.13) in various scattering experiments at different angles $\Delta\xi$, of the optical collection. The most important case is the depolarized measurements at right angles. If we plot the angular functions that act like coefficients in eq.-

(2.4.8a) versus $\Delta\xi$ we obtain the graph depicted in fig. (2.4). We see that the biggest term corresponds to the third one in eq. (2.4.13b) because the coefficient that affects the molecular property tensors posesses a higher order of magnitude than the others. But C, eq. (2.4.9a) is the numerator of $\Delta_{dep}(90^{0})$ in eqs. (2.3.15), so there is no change in the interpretation of the CID-spectra in terms of the polarizability and optical activity tensors. We also notice that the artifacts are dropped, which happens because their coefficients in the depolarized scattering at right angles are two or three orders of magnitude lower than the other one.

It is a very good approximation to write, when $\Delta\xi$ is very small ($\longrightarrow 0$), the angles, $\Delta\xi$, instead of their respective sine functions, $\sin(\Delta\xi)$. Therefore we shall obtain,

1.- Forward scattering,

$$W^R - W^L = MPR^2 \frac{\pi}{c} \Delta^2\xi \left(3\alpha_{\alpha\alpha} G'_{\beta\beta} + \alpha_{\alpha\beta} G'_{\alpha\beta} - \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}\right). \quad (2.4.14)$$

2.- Backward scattering,

$$W^R - W^L = MPR^2 \frac{4\pi}{c} \Delta^2\xi \left(3\alpha_{\alpha\beta} G'_{\alpha\beta} - \alpha_{\alpha\alpha} G'_{\beta\beta} + \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}\right). \quad (2.4.15)$$

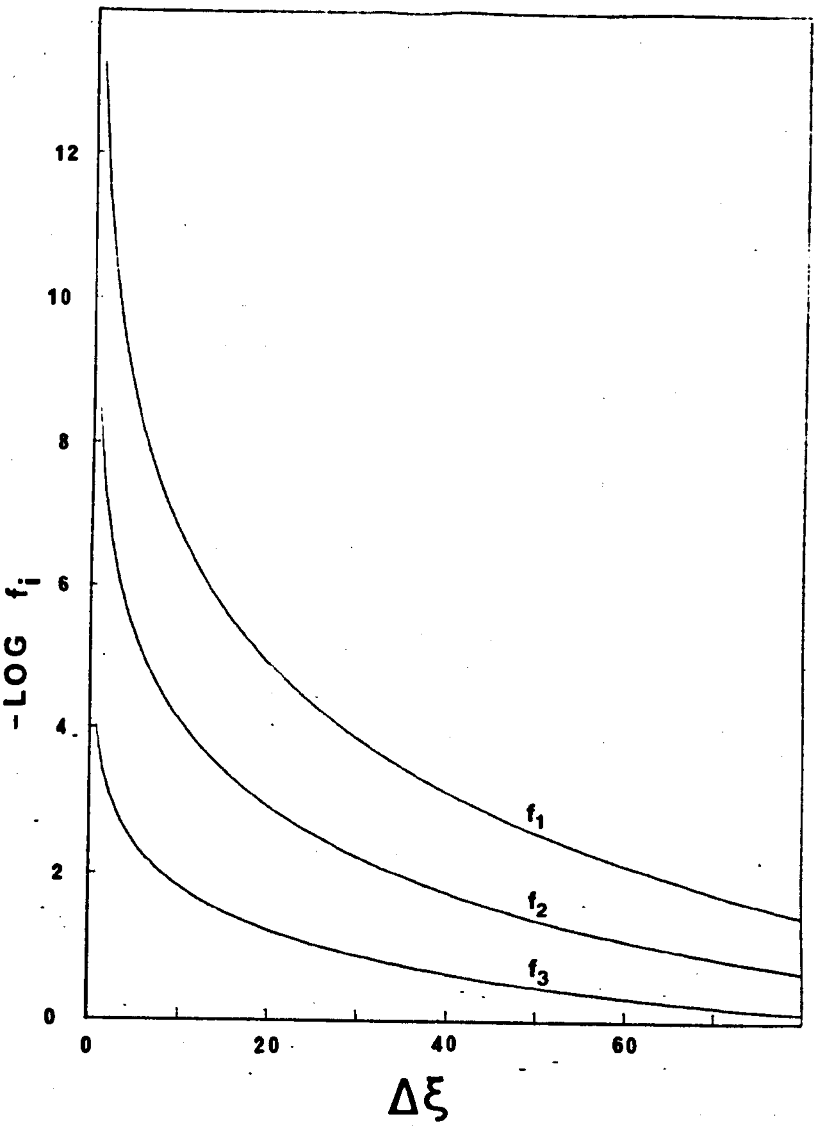
3.- Scattering at right angles.

3.1- Depolarized,

$$W^R_{yd} - W^L_{yd} = 2MPR^2 \frac{4}{c} \Delta^2\xi \left(3\alpha_{\alpha\beta} G'_{\alpha\beta} - \alpha_{\alpha\alpha} G'_{\beta\beta} - \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}\right). \quad (2.4.16a)$$

3.2- Polarized,

$$W^R_{xd} - W^L_{xd} = 4MPR^2 \, \Delta^2\xi \Big[-2\left(\frac{1}{c} - 1\right)\left(\beta^2 + \frac{5}{3}\beta'^2\right)\delta \cos(+)\cos(-) \quad (2.4.16b)$$
$$+ \frac{1}{c}\left(7\alpha_{\alpha\beta} G'_{\alpha\beta} + \alpha_{\alpha\alpha} G'_{\beta\beta} + \frac{\omega}{3} \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}\right)\Big].$$



<u>Figure</u> <u>2.4</u>.-Plot of $-\log[f_i(\Delta\xi)]$ v.s. $\Delta\xi$. These functions are:

$$f_1(\Delta\xi) = 1/3\ \sin^3(\Delta\xi/2)\ (\Delta\xi - \sin\Delta\xi),$$
$$f_2(\Delta\xi) = 1/3\ \sin^3(\Delta\xi/2)\ (\Delta\xi + \sin\Delta\xi),$$
$$f_3(\Delta\xi) = \Delta\xi\ [\sin(\Delta\xi/2) - 1/3\ \sin^3(\Delta\xi/2)].$$

They are the coefficients of the polarizability and optical activity tensors.

The first two cases have no contribution from optical artifacts at any $\Delta\xi$. In the depolarized case the artifacts are negligible for collection optic, $\Delta\xi$, smaller than 50° where artifacts can affect by 10% or higher. For the polarized scattering at right angles there is always contribution of artifacts in the same order of magnitude as $\Delta_{pol}(90^{\circ})$ and they only can be removed either with very good modulation or considering a double lens collection optic as described by Hug (1981). Also relevant is the influence of the depolarization ratio, ϱ, which will affect differently each band in the spectrum.

We shall write the equations of the CPD in the case of a circular lens when $\Delta\xi \leq 10^{\circ}$, in terms ofthe polarizability and optical activity tensors explicitly. From eqs. (2.4.6,8),

1.- Forward scattering,

$$\nabla(0^{\circ}) = \Delta(0^{\circ}) . \qquad (2.4.17)$$

2.- Backward scattering,

$$\nabla(180^{\circ}) = \Delta(180^{\circ}). \qquad (2.4.18)$$

3.- Scattering at right angles.

3.1.- Depolarized,

$$\nabla_{dep}(90^{\circ}) = \Delta_{dep}(90^{\circ}). \qquad (2.4.19a)$$

3.2.- Polarized,

$$\nabla_{pol}(90^{\circ}) = -18\left(\frac{1-\varrho}{1+\varrho}\right)\delta\cos(+)\cos(-) + \Delta_{pol}(90^{\circ}). \qquad (4.19.b)$$

We can appreciate that the terms corresponding to the molecular property tensors have not changed, including artifacts, in the three first cases with respect to the numerator of the well established equations of the CID,... but now we know under what experimental conditions.

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3 THE GENERALIZED TWO-GROUP MODEL

The VROA equations will now be developed in a computational form. The two-group model and the bond-polarizability theory have been used. An extension to non-axially symmetric bonds is proposed. The restrictions of this approximation are also discussed. For a general background on molecular vibrations we shall refer to Califano (1972) and Wilson et al. (1955).

3.1 The bond-polarizability theory applied to VROA.

The bond-polarizability theory of intensities is an approximate method for calculation of intensities in Raman spectroscopy. It was originally proposed by Vol'kenshtein (1941) and later extended by Vol'kenshtein et al. (1949). The valence-optical approach stems from the concept of additivity of various molecular properties. A property of a molecule can be represented as a sum of the properties of the several structural units which are preserved on passing from one molecule to another. The bonds of a molecule are generally regarded as these structural units. It should be emphasized that the constituent structural units cannot be defined in an abstract way: the definition must closely rely on the experimental findings. In the vibrational spectra, the additivity is often seen to break down, and this effect can be generally attributed to "coupling" or interaction between the structural units. Consequently, sometimes the chemical bonds cannot be considered the basic structural units of the molecule, being neccesary more complex groups to be dealt with. The additivity hypothesis associated with the use of chemical bonds is considered as the "zero" approximation of the valence optical theory. This hypothesis assigns an independent polarizability tensor $\alpha_{i\alpha\beta}$ to each i-th chemical bond, and the overall polarizability is taken equal to the sum of the polarizabilities of the individuals bonds,

$$\alpha_{\alpha\beta} = \sum_{i=1}^{N} \alpha_{i\alpha\beta} , \tag{3.1.1}$$

where N is the total number of chemical bonds.

Within Placzek's approximation for the vibrational transition polarizability at transparent frequencies, the effective polarizability operator $\alpha_{\alpha\beta}$ is a function of the normal vibrational coordinates, $\alpha_{\alpha\beta}(Q)$, so expanding in Taylor's series we get,

$$\langle m_v|\alpha_{\alpha\beta}(Q)|n_v\rangle = \alpha^o_{\alpha\beta}\,\delta_{m_v n_v} + \sum_p \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_o \langle m_v|Q_p|n_v\rangle + \frac{1}{2}\sum_{p,q}\left(\frac{\partial^2\alpha_{\alpha\beta}}{\partial Q_p\partial Q_q}\right)_o \langle m_v|Q_pQ_q|n_v\rangle + \dots , \tag{3.1.2}$$

with $\alpha^o_{\alpha\beta}$ as the molecular polarizability at the equilibrium nuclear configuration within the ground electronic state. The second term describes fundamental transitions and the third term describes first overtone and combination transitions. $<n_v|$ and $<m_v|$ denote the ground state and the first excited state associated with the normal mode Q_p, then

$$\langle 1_p|Q_p|0\rangle = \left(\frac{\hbar}{2\omega_p}\right)^{1/2} , \tag{3.1.3}$$

and ω_p is the angular frequency that corresponds to the transition $<1_p| \leftarrow <0|$.

We can describe the polarizability in terms of internal vibrational coordinates, s_q, that can be written as a function of the normal coordinates of vibration,

$$\underset{\sim}{s} = \underset{\sim}{L}\,\underset{\sim}{Q}. \tag{3.1.4}$$

Then the matrix elements associated with the first vibrational transition of the polarizability operator with respect to the normal coordinate Q_p is, using (3.1.1) to (3.1.4)

$$\langle 1_p|\alpha_{\alpha\beta}(Q)|0\rangle = \sqrt{\frac{\hbar}{2\omega_p}}\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp} \quad . \tag{3.1.5}$$

Now we have to extend the bond polarizability theory to the optical activity tensors $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$; also we have to include the origin dependent part of each bond. All of this leads us to:

$$G'_{\alpha\beta}(Q) = \sum_i G'_{i\alpha\beta}(Q) - \frac{\omega}{2}\,\varepsilon_{\beta\gamma\delta}\sum_i R_{i\gamma}(Q)\,\alpha_{i\alpha\delta}(Q) \ , \tag{3.1.6a}$$

$$A_{\alpha\beta\gamma}(Q) = \sum_i \left[A_{i\alpha\gamma\delta}(Q) + \frac{3}{2}R_{i\beta}(Q)\alpha_{i\alpha\gamma}(Q) + \frac{3}{2}R_{i\gamma}(Q)\alpha_{i\alpha\beta}(Q) - R_{i\delta}(Q)\,\alpha_{i\alpha\delta}(Q)\delta_{\beta\gamma}\right], \tag{3.1.6b}$$

with $\underset{\sim}{R}_i$ as the vector from the molecular origin to the local origin of the i-th bond. Expanding each term in the vibrational normal coordinates and using (3.1.3-4) into (3.1.6a,b) it is obtained,

$$\begin{aligned}\langle 1_p|G'_{\alpha\beta}(Q)|0\rangle = \sqrt{\frac{\hbar}{2\omega_p}}&\left\{\sum_i\sum_q\left(\frac{\partial G'_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right.\\ &\left.-\frac{\omega}{2}\,\varepsilon_{\beta\gamma\delta}\sum_i\sum_q\left[R^0_{i\gamma}\left(\frac{\partial\alpha_{i\alpha\delta}}{\partial S_q}\right)_0 + \alpha^0_{i\alpha\delta}\left(\frac{\partial R_{i\gamma}}{\partial S_q}\right)_0\right]L_{qp}\right\},\end{aligned} \tag{3.1.7a}$$

$$\begin{aligned}\langle 1_p|\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}(Q)|0\rangle = \sqrt{\frac{\hbar}{2\omega_p}}\,\varepsilon_{\alpha\gamma\delta}&\left\{\sum_i\sum_q\left(\frac{\partial A_{i\gamma\delta\beta}}{\partial S_q}\right)_0 L_{qp}\right.\\ &+\sum_i\sum_q\left[\frac{3}{2}R^0_{i\delta}\left(\frac{\partial\alpha_{i\gamma\delta}}{\partial S_q}\right)_0 + \frac{3}{2}\alpha^0_{i\gamma\delta}\left(\frac{\partial r_{i\gamma}}{\partial S_q}\right)_0 - R^0_{i\epsilon}\left(\frac{\partial\alpha_{i\gamma\epsilon}}{\partial S_q}\right)_0\delta_{\gamma\beta}\right.\\ &\left.\left.-\alpha^0_{i\gamma\epsilon}\left(\frac{\partial r_{i\epsilon}}{\partial S_q}\right)_0\delta_{\delta\beta}\right]L_{qp}\right\} \ .\end{aligned} \tag{3.1.7b}$$

Using the expressions (3.1.5-7) we can obtain the required products that determine the Raman intensity and the CID:

$$\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|\alpha_{\alpha\beta}|0\rangle = \frac{\hbar}{2\omega_p}\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right]^2, \qquad (3.1.8a)$$

$$\langle 0|\alpha_{\alpha\alpha}|1_p\rangle\langle 1_p|\alpha_{\beta\beta}|0\rangle = \frac{\hbar}{2\omega_p}\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\alpha}}{\partial S_q}\right)_0 L_{qp}\right]\left[\sum_j\sum_r\left(\frac{\partial\alpha_{j\beta\beta}}{\partial S_r}\right)_0 L_{rp}\right], \qquad (3.1.8b)$$

$$\begin{aligned}\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|G'_{\alpha\beta}|0\rangle = {} & \frac{\hbar}{2\omega_p}\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right]\left[\sum_j\sum_r\left(\frac{\partial G'_{j\alpha\beta}}{\partial S_r}\right)_0 L_{rp}\right] \\ & -\frac{\hbar\omega}{4\omega_p}\varepsilon_{\beta\gamma\delta}\left\{\sum_{i<j}R^0_{ji_\gamma}\left[\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)L_{qp}\right]\left[\sum_r\left(\frac{\partial\alpha_{j\alpha\delta}}{\partial S_r}\right)_0 L_{rp}\right]\right. \\ & \left.+\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)L_{qp}\right]\left[\sum_j\sum_r\alpha^0_{j\delta\alpha}\left(\frac{\partial R_{j\gamma}}{\partial S_r}\right)_0 L_{rp}\right]\right\},\end{aligned}$$

(3.1.8c)

$$\begin{aligned}\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|\tfrac{\omega}{3}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}|0\rangle = {} & \frac{\hbar\omega}{6\omega_p}\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right]\left[\varepsilon_{\alpha\gamma\delta}\sum_j\sum_r\left(\frac{\partial A_{j\gamma\delta\beta}}{\partial S_r}\right)_0 L_{rp}\right] \\ & -\frac{\hbar\omega}{4\omega_p}\varepsilon_{\beta\gamma\delta}\left\{\sum_{i<j}R^0_{ji_\gamma}\left[\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right]\left[\sum_r\left(\frac{\partial\alpha_{j\delta\alpha}}{\partial S_r}\right)_0 L_{rp}\right]\right. \\ & \left.+\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial S_q}\right)_0 L_{qp}\right]\left[\sum_j\sum_r\alpha^0_{j\delta\alpha}\left(\frac{\partial R_{j\gamma}}{\partial S_r}\right)_0 L_{rp}\right]\right\},\end{aligned}$$

(3.1.8d)

$$\langle 0|\alpha_{\alpha\alpha}|1_p\rangle\langle 1_p|G'_{\beta\beta}|0\rangle = \frac{\hbar}{2\omega_p}\left[\sum_i\sum_q\left(\frac{\partial\alpha_{i\alpha\alpha}}{\partial S_q}\right)_0 L_{qp}\right]\left[\sum_j\sum_r\left(\frac{\partial G'_{j\beta\beta}}{\partial S_r}\right)_0 L_{rp}\right],$$

(3.1.8e)

(Barron, 1979). Here the first term in (3.1.8c,d) corresponds to products of intrinsic group polarizability and optical activity tensors. The second and third terms are identical in both equations: the second one represents a generalization of the two-group mechanism with $\mathbf{R}^0_{ij} = \mathbf{R}^0_i - \mathbf{R}^0_j$, where $\mathbf{R}^0_{i,j}$ is the vector position of the group i (or j) with respect to the molecular origin at the equilibrium configuration; the third term is a generalization of the inertial mechanism (Barron and Buckingham, 1979).

These VROA expressions are invariant both to the choice of the molecular origin and the local group origin. The two-group and the inertial terms are generated by the origin-dependent parts of the total $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ tensors, so any changes in these terms caused by changes in the relative dispositions of the molecular origin and the local group origins are compensated by changes in the first terms of (3.1.8c,d).

If a bond has a threefold or higher rotation axis, its polarizability and optical activity tensors can be written in terms of components referred to principal axes as

$$\alpha_{i\alpha\beta} = \alpha_{i\perp}\delta_{\alpha\beta} + \Delta_i u_{i\alpha} u_{i\beta} , \qquad (3.1.9a)$$

$$G'_{i\alpha\beta} = G'_i \varepsilon_{\alpha\beta\gamma} u_{i\gamma} , \qquad (3.1.9b)$$

$$A_{i\alpha\beta\gamma} = \left(\tfrac{3}{2} A_{i\parallel} - 2 A_{i\perp}\right) u_{i\alpha} u_{i\beta} u_{i\gamma} + A_{i\parallel}\left(u_{i\beta}\delta_{\beta\gamma} + u_{i\gamma}\delta_{\alpha\beta}\right)$$
$$- A_{i\parallel} u_{i\alpha} \delta_{\beta\gamma} . \qquad (3.1.9c)$$

The axially-symmetric bonds give zero contribution to the VROA equations through the intrinsic bond optical activity tensors. If the origins are chosen to lie along the symmetry axes, all the Raman optical activity is generated by the two group and inertial terms in (3.1.8b and c). And these two-terms, taken together, are invariant to displacements of the local group origins along the symmetry axes; for it is easily verified by invoking (3.1.9a) for each group that the change in one term is compensated by an equal and opposite change in the other term. Notice that it is only changes in the inertial terms with $i \neq j$ that compensate changes in the two-group terms: intrinsic group inertial terms, corresponding to $i = j$, are invariant to the position of the origin anywhere along the symmetry axis.

3.2 Computational form of the VROA equations for axially-symmetric bonds.

If we consider that all the bonds are axially-symmetric in the molecule we can write the polarizability tensor of each one as in (3.1.9a) where $\Delta_i = \alpha_{i\parallel} - \alpha_{i\perp}$ is the polarizability anisotropy. In the zero-approximation of the valence optical approach $\alpha_{i\alpha\beta}$ depends only on the variation in the length of the i-th bond, then

$$\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial Q_p}\right)_0 = \sum_q \left(\frac{\partial\alpha_{i\alpha\beta}}{\partial s_q}\right)_0 L_{qp}$$

$$= \left[\left(\frac{\partial\alpha_{i\perp}}{\partial r_i}\right)_0 \delta_{\alpha\beta} + \left(\frac{\partial\Delta_i}{\partial r_i}\right)_0 u_{i_\alpha} u_{i_\beta}\right] L_{r_i p} + \Delta_i \sum_q \left[\frac{\partial(u_{i_\alpha} u_{i_\beta})}{\partial s_q}\right]_0 L_{qp} \,. \qquad (3.2.1)$$

Here $L_{r_i p}$ is the matrix element of $\underset{\sim}{L}$ associated with the stretch of bond i. In the second term the summation is extended over all the internal coordinates q.

The next step is to solve the derivatives of the bond unit vectors with respect to the internal coordinates. Let us suppose that the i-th bond goes from atom b to atom a, so that the instantaneous unit vector $\underset{\sim}{u}_i$ is

$$\underset{\sim}{u}_i = (\underset{\sim}{R}_a - \underset{\sim}{R}_b)/|\underset{\sim}{R}_a - \underset{\sim}{R}_b|. \qquad (3.2.2)$$

If $\underset{\sim}{r}_m$ is the instantaneous displacement vector of atom m, then the position vector of atom m with respect to the molecular origin is $\underset{\sim}{R}_m = \underset{\sim}{R}^o_m + \underset{\sim}{r}_m$. The cartesian displacement of an atom in matrix notation is (Califano, 1972)

$$\underset{\approx}{r} = \underset{\sim}{M}^{-1} \underset{\approx}{B} \underset{\sim}{G}^{-1} \underset{\sim}{s}, \qquad (3.2.3)$$

where $\underset{\sim}{M}^{-1}$ is the matrix of inverse masses, $\underset{\approx}{B}$ is the B-matrix of the Wilson vectors, $\underset{\sim}{G}^{-1}$ is the inverse kinetic energy matrix and s the internal coordinate matrix. If we particularize to atom m we get,

$$r_{m\beta} = \varepsilon_m \sum_{t,k} \tilde{S}_{mt\beta} (G^{-1})_{tk} s_k, \qquad (3.2.4)$$

where ε_m is an element of the $\underset{\sim}{M}^{-1}$, $\tilde{\underset{\sim}{s}}_{mt}$ is the transpose Wilson's vector associated with atom m and internal coordinate s_t. The summation is extended over all internal coordinates. From (3.2.4) we can write:

$$\left(\frac{\partial r_{m\beta}}{\partial s_q}\right)_0 = \varepsilon_m \sum_t \tilde{S}_{mt\beta} (G^{-1})_{tq} . \qquad (3.2.5)$$

Now we can manage the derivatives $(\partial u_i/\partial s_q)_o$, so:

$$\left(\frac{\partial u_{i\alpha}}{\partial s_q}\right)_0 = \left(\frac{\partial u_{i\alpha}}{\partial r_{a\beta}}\right)_c \left(\frac{\partial r_{a\beta}}{\partial s_q}\right)_c + \left(\frac{\partial u_{i\alpha}}{\partial r_{b\beta}}\right)_c \left(\frac{\partial r_{b\beta}}{\partial s_q}\right)_0 . \qquad (3.2.6)$$

Deriving eq. (3.2.2) it is not difficult to show

$$\left(\frac{\partial u_{i\alpha}}{\partial r_{a\beta}}\right)_c = -\left(\frac{\partial u_{i\alpha}}{\partial r_{b\beta}}\right)_c = \sigma_i \left(\delta_{\alpha\beta} - u^o_{i\alpha} u^o_{i\beta}\right), \qquad (3.2.7)$$

here we have done $\sigma_i = |\underset{\sim}{R}^o_a - \underset{\sim}{R}^o_b|^{-1}$, and we shall drop the superindex nought in the vectors $\underset{\sim}{u}_i$. Then substituting (3.2.7) and (3.2.5) into (3.2.6) we arrive to

$$\left(\frac{\partial u_{i\alpha}}{\partial s_q}\right)_0 = \sigma_i \left(\delta_{\alpha\beta} - u_{i\alpha}u_{i\beta}\right) \sum_t \left(\varepsilon_a \tilde{S}_{at_\beta} - \varepsilon_b \tilde{S}_{bt_\beta}\right)(G^{-1})_{tq} \; . \qquad (3.2.8)$$

At this stage we shall introduce a more concise notation:

$$\underset{\sim}{d}{}^t_m = \varepsilon_m \underset{\sim}{\tilde{S}}_{mt} \; , \qquad (3.2.9a)$$

$$\underset{\sim}{d}{}_i^t = \underset{\sim}{d}{}^t_a - \underset{\sim}{d}{}^t_b \; , \qquad (3.2.9b)$$

$$A^t_i = \underset{\sim}{u}_i \cdot \underset{\sim}{d}{}^t_i \; . \qquad (3.2.9c)$$

Then (3.2.8) becomes:

$$\left(\frac{\partial u_{i\alpha}}{\partial s_q}\right)_0 = \sigma_i \sum_t \left(d^t_{i\alpha} - u_{i\alpha} A^t_i\right)(G^{-1})_{tq} \; , \qquad (3.2.10)$$

Thereby (3.2.1) can be written as:

$$\left(\frac{\partial \alpha_{i\alpha\beta}}{\partial s_q}\right)_0 = \left(\alpha'_{i\perp}\delta_{\alpha\beta} + \Delta'_i \, u_{i\alpha}u_{i\beta}\right) L_{r_i p}$$
$$+ \sigma_i \Delta_i \sum_i \left(u_{i\beta} d^t_{i\alpha} + u_{i\alpha} d^t_{i\beta} - 2 u_{i\alpha} u_{i\beta} A^t_i\right)(L^{-1})_{pt} , \qquad (3.2.11)$$

We have used the well known relationship $\underset{\sim}{G} = \underset{\sim}{L}\underset{\sim}{\tilde{L}}$, where $(L^{-1})_{pt}$ an element of the inverse eigenvector L-matrix associated with internal coordinate s_t and normal coordinate Q_p. Here we have changed the notation α'_i = $(\partial\alpha_{i\perp}/\partial r_i)_0$ and Δ'_i = $(\partial\Delta_i/\partial r_i)_0$.

To deal with the inertial term we need the derivatives of the positional vector of each group with respect to the internal coordinates. If we choose atom b of each bond as the bond origin, then using (3.2.5) and (2.2.9a) we obtain,

$$\sum_r \left(\frac{\partial R_{j\gamma}}{\partial s_r}\right)_0 L_{rp} = \sum_r d^r_{j\gamma} (L^{-1})_{pr} \; . \qquad (3.2.12)$$

Then with (3.2.11) and (3.2.12), principally, we can get the different products (3.1.8a,e) in computational form, but only in the case in which all bonds are considered axially symmetric:

$$\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|\alpha_{\alpha\beta}|0\rangle = \frac{\hbar}{2\omega_p}\Big\{\sum_i\Big[(\alpha'_{i\perp}\delta_{\alpha\beta}+u_{i_\alpha}u_{i_\beta}\Delta'_i)L_{r_ip}$$
$$+\sigma_i\Delta_i\sum_q(u_{i_\alpha}d^q_{i_\alpha}+u_{i_\beta}d^q_{i_\beta}-2u_{i_\alpha}u_{i_\beta}A^q_i)(L^{-1})_{pq}\Big]\Big\}^2 \quad (3.2.13a)$$

$$\langle 0|\alpha_{\alpha\alpha}|1_p\rangle\langle 1_p|\alpha_{\beta\beta}|0\rangle = \frac{\hbar}{2\omega_p}\Big[\sum_i(3\alpha'_{i\perp}+\Delta'_i)L_{r_ip}\Big]^2, \quad (3.2.13b)$$

$$\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|G'_{\alpha\beta}|0\rangle = \langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|\frac{\omega}{3}\,\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}|0\rangle$$
$$= -\frac{\hbar\omega}{4\omega_p}\varepsilon_{\beta\gamma\delta}\Big\{\sum_{i<j}R^0_{ji\gamma}\Big[u_{i_\alpha}u_{i_\beta}\Delta_i L_{r_ip}+\sigma_i\Delta_i\sum_q(u_{i_\beta}d^q_{i_\alpha}+u_{i_\alpha}d^q_{i_\beta}$$
$$-2u_{i_\alpha}u_{\beta}A^q_i)(L^{-1})_{pq}\Big]\Big[u_{j_\delta}u_{j_\alpha}\Delta'_j L_{r_jp}+\sigma_j\Delta_j\sum_r(u_{j_\alpha}d^r_{j_\delta}+u_{j_\delta}d^q_{j_\alpha}$$
$$-2u_{j_\alpha}u_{j_\delta}A^r_j)(L^{-1})_{pr}\Big]+\sum_{i,j}\Big[u_{i_\alpha}u_{i_\beta}\Delta'_i L_{r_ip}+\sigma_i\Delta_i\sum_q(u_{i_\alpha}d^q_{i_\beta}+u_{\beta}d^q_{i_\alpha}$$
$$-2u_{i_\alpha}u_{i_\beta}A^q_i)(L^{-1})_{pq}\Big]\Delta_j u_{j_\alpha}u_{j_\delta}\sum_r d^r_{b_\gamma}(L^{-1})_{pr}\Big\}, \quad (3.2.13c)$$

$$\langle 0|\alpha_{\alpha\alpha}|1_p\rangle\langle 1_p|G'_{\beta\beta}|0\rangle = 0. \quad (3.2.13d)$$

In (3.2.13.c) we have eliminated all the Kronecker deltas because $\varepsilon_{\beta\gamma\delta}\delta_{\alpha\beta}\delta_{\delta\alpha} = 0$ and $\varepsilon_{\beta\gamma\delta}\delta_{\alpha\beta}u_\alpha u_\delta = 0$. All of these equations have been previously derived (Clark, 1981; Barron and Clark, 1982) but some differences have been found ,(3.2.4) and (3.2.11), which will affect later calculations.

3.3 Extension to non-axially symmetric bonds.

Now we shall reduce the symmetry of the bonds within the molecule, which is the case of the carbonyl group, for instance. Let us consider bonds labelled with i to be axially symmetric and bonds with i′ to have internal symmetry C_{2v} or lower. Then, the tensor products $\alpha_{\alpha\beta}T_{\alpha\beta}$, where $T_{\alpha\beta}$ is $G'_{\alpha\beta}$ or $\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}$, are:

$$\begin{aligned}\langle 0|\alpha_{\alpha\beta}|1_p\rangle\langle 1_p|T_{\alpha\beta}|0\rangle &= \frac{\hbar}{2\omega_p}\left[\sum_i\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial Q_p}\right)_0+\sum_{i'}\left(\frac{\partial\alpha_{i'\alpha\beta}}{\partial Q_p}\right)_0\right]\left[\sum_j\left(\frac{\partial T_{j\alpha\beta}}{\partial Q_p}\right)_0+\sum_{j'}\left(\frac{\partial T_{j'\alpha\beta}}{\partial Q_p}\right)_0\right]\\ &= \frac{\hbar}{2\omega_p}\left[\sum_{i,j}\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial Q_p}\right)_0\left(\frac{\partial T_{j\alpha\beta}}{\partial Q_p}\right)_0+\sum_{i,j'}\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial Q_p}\right)_0\left(\frac{\partial T_{j'\alpha\beta}}{\partial Q_p}\right)_0\right.\\ &\qquad\left.+\sum_{i',j}\left(\frac{\partial\alpha_{i'\alpha\beta}}{\partial Q_p}\right)_0\left(\frac{\partial T_{j\alpha\beta}}{\partial Q_p}\right)_0+\sum_{i',j'}\left(\frac{\partial\alpha_{i'\alpha\beta}}{\partial Q_p}\right)_0\left(\frac{\partial T_{j'\alpha\beta}}{\partial Q_p}\right)_0\right].\end{aligned}\tag{3.3.1}$$

Here the non-dashed sums correspond to eqs. (3.2.13a-d). We shall design an equation for bonds with C_{2v} symmetry. Let us work with the carbonyl group although this example is also valid for groups such as >C=CH$_2$ or >N=O. If we suppose that the C_{2v}-symmetry is maintained during a vibration, the only non-zero components of $\alpha_{\alpha\beta}$, $G'_{\alpha\beta}$ and $\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}$ are:

$$\alpha_{\alpha\beta} = \alpha_{xx}I_\alpha I_\beta + \alpha_{yy}J_\alpha J_\beta + \alpha_{zz}K_\alpha K_\beta\,, \tag{3.3.2a}$$

$$G'_{\alpha\beta} = G'_{xy}I_\alpha J_\beta + G'_{yx}J_\alpha I_\beta\,, \tag{3.3.2b}$$

$$\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} = (A_{yzy}-A_{zyy})I_\alpha J_\beta + (A_{zxx}-A_{xzx})J_\alpha I_\beta\,. \tag{3.3.2c}$$

The intrinsic set of orthogonal vectors ($\underset{\sim}{I}$, $\underset{\sim}{J}$, $\underset{\sim}{K}$) to the carbonyl group are, [see fig. (3.1)]

$$I_\alpha = a\,\varepsilon_{\alpha\beta\gamma}u_{2\beta}u_{1\gamma} - b\,u_{0\alpha}\,, \tag{3.3.3a}$$

$$J_\alpha = a\,u_{0\beta}(u_{2\alpha}u_{1\beta} - u_{1\alpha}u_{2\beta})\,, \tag{3.3.3b}$$

$$K_\alpha = u_{0\alpha}\,, \tag{3.3.3c}$$

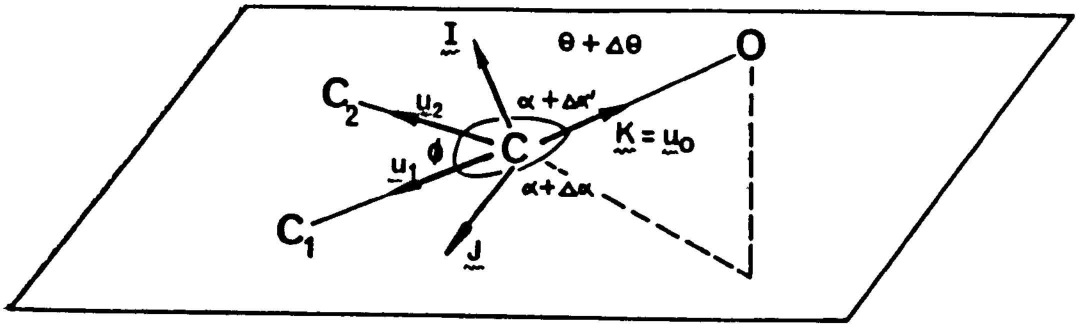

Figure 3.1.- Arbitrary movement of the >C=O group. The plane C_1CC_2 is considered as reference.

where $a = [\sin\phi \sin(\theta + \Delta\theta)]^{-1}$ and $b = [\mathrm{tg}(\theta + \Delta\theta)]^{-1}$.

Then (3.3.2a,b) become

$$\alpha_{\alpha\beta} = \alpha_{xx}(a\,\varepsilon_{\alpha\gamma\delta} u_{2_\gamma} u_{1_\delta} - b\,u_{0_\alpha})(-a\,\varepsilon_{\lambda\beta\mu} u_{2_\lambda} u_{1_\mu} - b\,u_{0_\beta})$$

$$+ \alpha_{yy} a^2 u_{0_\gamma}(u_{2_\alpha} u_{1_\gamma} - u_{1_\gamma} u_{2_\gamma}) \cdot u_{0_\delta}(u_{2_\beta} u_{1_\delta} - u_{1_\beta} u_{2_\delta}) + \alpha_{zz} u_{0_\alpha} u_{0_\beta} , \tag{3.3.4a}$$

$$G'_{\alpha\beta} = G'_{xy}\left(a\,\varepsilon_{\alpha\gamma\delta}\,u_{2\gamma}\,u_{1\delta} - b\,u_{0\alpha}\right) a\,u_{0\lambda}\left(u_{2\beta}u_{1\lambda} - u_{1\beta}u_{2\lambda}\right)$$

$$+ G'_{yx}\left(a\,\varepsilon_{\beta\gamma\delta}\,u_{2\gamma}\,u_{1\delta} - b\,u_{0\beta}\right) a\,u_{0\lambda}\left(u_{2\alpha}u_{1\lambda} - u_{1\alpha}u_{2\lambda}\right). \quad (3.3.4b)$$

We shall define a new vector in order to reduce notation,

$$h^{q}_{i\alpha} = \sigma_i\left(d^{q}_{i\alpha} - A^{q}_{i}\,u_{i\alpha}\right). \quad (3.3.5)$$

Within Placzek's approximation we can drop the antisymmetric part of the $G'_{\alpha\beta}$ tensor, then

$$\left(\frac{\partial G'_{\alpha\beta}}{\partial Q_p}\right)_0 = \frac{1}{2}\left[\frac{\partial}{\partial Q_p}\left(G'_{\alpha\beta} + G'_{\beta\alpha}\right)\right]_0$$

$$= \frac{1}{2}\left(G'_{xy} + G'_{yx}\right)\sum_r\left[\frac{\partial}{\partial S_r}\left(I_\alpha J_\beta + I_\beta J_\alpha\right)\right]_0 L_{rp}. \quad (3.3.6)$$

where it has been assumed that G'_{xy} and G'_{yx} remain constant during the course of a vibration. The derivatives of the polarizability and optical activity tensor with respect to the normal coordinate of vibration Q_p become,

$$\left(\frac{\partial \alpha_{\alpha\beta}}{\partial Q_p}\right)_0 = \alpha_{xx}\sum_r\Big\{\left(-a^0\varepsilon_{\lambda\beta\mu}u_{2\lambda}u_{1\mu} - b^0 u_{0\beta}\right)\left[a^0\varepsilon_{\alpha\gamma\delta}\left(h^r_{2\gamma}u_{1\delta} + h^r_{1\delta}u_{1\gamma}\right) - b^0 h^r_{0\alpha}\right]$$

$$+\left(a^0\varepsilon_{\alpha\gamma\delta}u_{2\gamma}u_{1\delta} - b^0 u_{0\alpha}\right)\left[-a^0\varepsilon_{\lambda\beta\mu}\left(h^r_{2\lambda}u_{1\mu} + h^r_{1\mu}u_{2\lambda}\right) - b^0 h^r_{0\beta}\right]\Big\}(L^{-1})_{pr}$$

$$+ \alpha_{yy}\sum_r a^{02}\Big\{\Big[h^r_{0\delta}\left(u_{2\beta}u_{1\delta} - u_{1\beta}u_{2\delta}\right) + u_{0\gamma}\big(h^r_{2\beta}u_{1\delta} + h^r_{1\delta}u_{2\beta} - h^r_{1\beta}u_{2\delta}$$

$$- h^r_{2\delta}u_{1\beta}\big)\Big]u_{0\gamma}\left(u_{2}\;u_{1\gamma} - u_{1\alpha}u_{2\gamma}\right) + \Big[h^r_{0\gamma}\left(u_{2\alpha}u_{1\gamma} - u_{1\alpha}u_{2\gamma}\right)$$

$$+ u_{0\gamma}\left(h^r_{2\alpha}u_{1\gamma} + h^r_{1\gamma}u_{2\alpha} - h^r_{1\alpha}u_{2\gamma} - h^r_{2\gamma}u_{1\alpha}\right)\Big]u_{0\delta}\left(u_{2\beta}u_{1\delta} - u_{1\beta}u_{2\delta}\right)\Big\}(L^{-1})_{pr}$$

$$+ \alpha_{zz}\sum_r\left(h^r_{0\alpha}u_{0\beta} + h^r_{0\beta}u_{0\alpha}\right)(L^{-1})_{pr} + \left(\alpha'_{xx}I_\alpha I_\beta + \alpha'_{yy}J_\alpha J_\beta + \alpha'_{zz}K_\alpha K_\beta\right)(L^{-1})_{pr\omega}$$

$$(3.3.7a)$$

$$\begin{aligned}
\left(\frac{\partial G'_{\alpha\beta}}{\partial Q_p}\right)_0 = \frac{1}{2}\left(G'_{xy}+G'_{yx}\right)\sum_r\Big\{&\left[a^{o2}\varepsilon_{\alpha\gamma\delta}\left(h^r_{2\gamma}u_{1\delta}+h^r_{1\delta}u_{2\gamma}\right)-a^o b^o h^r_{0\alpha}\right]u_{0\lambda}\left(u_{2\beta}u_{1\lambda}-u_{2\lambda}u_{1\beta}\right)\\
&+\left[a^{o2}\varepsilon_{\beta\gamma\delta}\left(h^r_{2\gamma}u_{1\delta}+h^r_{1\delta}u_{2\gamma}\right)-a^o b^o h^r_{0\beta}\right]u_{0\lambda}\left(u_{2\alpha}u_{1\lambda}-u_{2\lambda}u_{1\alpha}\right)\\
&+\left[h^r_{0\lambda}\left(u_{2\beta}u_{1\lambda}-u_{1\beta}u_{2\lambda}\right)+u_{0\lambda}\left(u_{1\lambda}h^r_{2\beta}+u_{2\beta}h^r_{1\lambda}-u_{1\beta}h^r_{2\lambda}-u_{2\lambda}h^r_{1\beta}\right)\right]\\
&\times\left(a^{o2}\varepsilon_{\alpha\gamma\delta}u_{2\lambda}u_{1\delta}-a^o b^o u_{0\alpha}\right)+\left[h^r_{0\lambda}\left(u_{2\alpha}u_{1\lambda}-u_{1\alpha}u_{2\lambda}\right)\right.\\
&\left.+u_{0\lambda}\left(u_{1\lambda}h^r_{2\alpha}+u_{2\alpha}h^r_{1\lambda}-u_{1\alpha}h^r_{2\lambda}-u_{2\lambda}h^r_{1\alpha}\right)\right]\left(-a^{o2}\varepsilon_{\beta\gamma\delta}u_{2\gamma}u_{1\delta}-a^o b^o u_{0\beta}\right)\Big\}(L^{-1})_{pr}\\
&+\frac{1}{2}\left[\frac{\partial}{\partial r_{co}}\left(G'_{xy}+G'_{yx}\right)\right]_0\left(I_\alpha J_\beta+I_\beta J_\alpha\right)(L^{-1})_{pr_{co}}\ ,
\end{aligned}$$

(3.3.7b)

$$\begin{aligned}
\varepsilon_{\alpha\gamma\delta}\left(\frac{\partial A_{\gamma\delta\beta}}{\partial Q_p}\right)_0 &= \frac{1}{2}\left(A_{yzy}-A_{zyy}+A_{zxx}-A_{xzy}\right)M\\
&\quad+\frac{1}{2}\left[\frac{\partial}{\partial r_{co}}\left(A_{yzy}-A_{zyy}+A_{zxx}-A_{xzy}\right)\right]_0\left(I_\alpha J_\beta+I_\beta J_\alpha\right)\ ,
\end{aligned}$$

(3.3.7c)

where M is the coefficient of $1/2(G'_{xy} + G'_{yx})$ in (3.3.7b). We have developed the contributions of the intrinsic optical activity tensors in (3.1.8b,c). Now eqs. (3.3.7a, c) together with (3.2.12) would be substituted into (3.1.8a,e), and we should arrive at the computational form of the CID equations in VROA, when one of the bonds has a C_{2v} internal symmetry. There is not much problem in extending this development to more than one non-axially symmetric bond. We realised that a lowering of the symmetry in the bonds leads us to an increase in the number of electrooptical parameters required, as well as to requiring a knowledge of the optical activity tensors. This arises because of the appearance of the intrinsic contribution from the optical activity tensors. In cases such as the allene or isocyanate groups, we can also use this formulation, provided the experimental parameters can be obtained. Further developments would have to include coupling terms and how they are affected by the normal coordinates of vibration. However, inclusion of these intrinsic optical activity contributions launch the required intermediate experimental parameters to an unacceptable level, and so they are not incorporated into the subsequent calculations. Thus in the molecules containing >C=O (Chapaters 7 and 8) we have assumed axial symmetry for this group since this is not very unrealistic.

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4 SECOND ORDER TRANSITIONS IN VROA

This chapter is devoted to the study of the influence of overtones and combination bands as well as the case of Fermi resonance. A correlation rule which relates polarized and depolarized spectra is proposed and previous experimental data show that it is qualitatively correct.

4.1 VROA of overtones and combination bands.

The state of the art of experimental VROA does not permit a clear study of overtone and combination bands; however it is interesting to know in advance how much will be its effect, what is its order of magnitude in comparison with the first order transition and what extra information we can extract. In order to deal with this problem we shall work, as we have done so far, within the Placzek approximation and with the bond polarizability model.

We know now that the third term of eq. (3.1.2) describes the second order transitions $|1_p 1_q\rangle \leftarrow |00\rangle$ and $|2_q\rangle \leftarrow |0\rangle$, associated with the transition polarizabilities (within the harmonic approximation)

$$\langle 2_p|\alpha_{\alpha\beta}(Q)|0\rangle = \frac{\hbar}{4\omega_p}\sum_i\left(\frac{\partial^2\alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 , \qquad (4.1.1a)$$

$$\langle 1_p 1_q|\alpha_{\alpha\beta}(Q)|00\rangle = \left(\frac{\hbar}{2\omega_p}\right)^{1/2}\left(\frac{\hbar}{2\omega_q}\right)^{1/2}\sum_i\left(\frac{\partial^2\alpha_{i\alpha\beta}}{\partial Q_p\partial Q_q}\right)_0 . \qquad (4.1.1b)$$

These arguments can be extended to the optical activity tensors $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$

$$\langle 2_p|G'_{\alpha\beta}(Q)|0\rangle = \frac{\hbar}{4\omega_p}\sum_i\left\{\left(\frac{\partial^2 G'_{i\alpha\beta}}{\partial Q_p^2}\right)_0 - \frac{\omega}{2}\,\varepsilon_{\beta\gamma\delta}\left[\left(\frac{\partial^2 r_{i\gamma}}{\partial Q_p^2}\right)_0 \alpha^0_{i\alpha\delta} + r^0_{i\gamma}\left(\frac{\partial^2\alpha_{i\alpha\delta}}{\partial Q_p^2}\right)_0\right]\right\} . \qquad (4.1.1c)$$

Equally we can obtain the matrix elements for a combination band. Analogous expressions are obtained for the matrix elements associated with $(\omega/3)\,\varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}$ from (3.1.6b).

The contributions to the isotropic Raman intensity and optical activity in the first overtone associated with the normal coordinates Q_p are found to be:

$$\langle 0|\alpha_{\alpha\beta}|2_p\rangle\langle 2_p|\alpha_{\alpha\beta}|0\rangle = \left(\frac{\hbar}{4\omega_p}\right)^2 \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 \alpha_{j\alpha\beta}}{\partial Q_p^2}\right)_0 , \tag{4.1.4a}$$

$$\langle 0|\alpha_{\alpha\alpha}|2_p\rangle\langle 2_p|\alpha_{\beta\beta}|0\rangle = \left(\frac{\hbar}{4\omega_p}\right)^2 \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\alpha}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 \alpha_{j\beta\beta}}{\partial Q_p^2}\right)_0 , \tag{4.1.4b}$$

$$\begin{aligned}\langle 0|\alpha_{\alpha\beta}|2_p\rangle\langle 2_p|G'_{\alpha\beta}|0\rangle = \left(\frac{\hbar}{4\omega_p}\right)^2 \Big\{ \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 G'_{j\alpha\beta}}{\partial Q_p^2}\right)_0 - \frac{\omega}{2}\varepsilon_{\beta\gamma\delta} \Big[\sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 \alpha_{j\alpha\beta}}{\partial Q_p^2}\right)_0 R_{ji\gamma} \\ + \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 r_{j\alpha\beta}}{\partial Q_p^2}\right)_0 \alpha^{\bullet}_{j\alpha\delta} \Big] \Big\} ,\end{aligned} \tag{4.1.4c}$$

$$\begin{aligned}\langle 0|\alpha_{\alpha\beta}|2_p\rangle\langle 2_p|\frac{\omega}{3}\varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}|0\rangle = \left(\frac{\hbar}{4\omega_p}\right)^2 \frac{\omega}{3} \Big\{ \varepsilon_{\alpha\gamma\delta} \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial A_{j\gamma\delta\beta}}{\partial Q_p^2}\right)_0 \\ - \frac{\omega}{2}\varepsilon_{\beta\gamma\delta} \Big[\sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 \alpha_{i\alpha\delta}}{\partial Q_p^2}\right)_0 R_{ij\gamma} + \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\beta}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 r_{i\gamma}}{\partial Q_p^2}\right)_0 \alpha^{\bullet}_{i\alpha\delta} \Big] \Big\} ,\end{aligned} \tag{4.1.4d}$$

$$\langle 0|\alpha_{\alpha\alpha}|2_p\rangle\langle 2_p|G'_{\beta\beta}|0\rangle = \left(\frac{\hbar}{4\omega_p}\right)^2 \sum_{i,j} \left(\frac{\partial^2 \alpha_{i\alpha\alpha}}{\partial Q_p^2}\right)_0 \left(\frac{\partial^2 G'_{j\beta\beta}}{\partial Q_p^2}\right)_0 . \tag{4.1.4e}$$

With respect to the combination levels the equations would be the same as in (4.1.4a,e) but substituting the factor $(\hbar/4\omega_p)$ by $(\hbar^2/4\omega_p\omega_q)$ and deriving partially with respect to Q_p and Q_q. We see that these equations have the same structure as the case of first order transitions (3.1.8), factors apart, although in these cases the third term in (4.1.4c,d) will not possess the meaning of "inertial term". The other terms remain within Barron's interpretation (Barron, 1982), but applied to second order transitions. It will be observed that eqs. (4.1.4a, e) have not been developed in terms of internal coordinates. This is because to deal with anharmonic terms it is neccesary to use curvilinear coordinates (Hoy, Mills and Strey; 1972). Sets of anharmonic force constants for chiral molecules are not known. The above equations show us that the VROA of these transitions are two orders of magnitude lower than in the corresponding first order transitions and to tackle them a very high sensitivity in the spectra will be required. Perhaps such observations could be a new source of information for cubic and quartic force constants. The development of these ideas are beyond the scope of this work.

4.2 Influence of Fermi Resonance in VROA.

We shall understand by Fermi resonance (FR) the accidental coincidence of vibrational energy levels in a polyatomic molecule. In such cases, if some symmetry conditions are fulfilled, a mutual perturbation sets in and, as a result, there is a redistribution of intensities between the two levels and both will repel each other. This phenomenon is recognized by the occurrence of two strong Raman bands in a frequency region where only one is expected.

In what follows we shall use the treatment of Suschinskii (1972) which is basically the formulation of Placzek (1934). A wide study within the bond polarizability theory has been recently carried out by Montero (1983).

We consider that E_m^o is an energy level with a two-fold degeneracy and $|1^o\rangle$, $|2^o\rangle$ are the associated eigenstates. We cannot decide what is the best eigenfunction that represents the system, so we choose a linear combination

$$|k\rangle = c_{k1}|1^o\rangle + c_{k2}|2^o\rangle, \qquad (4.2.1)$$

where the coefficients c_{k1} and c_{k2} are normalized. If H^o is the unperturbed hamiltonian and H' the perturbation term, then the equation

$$(H^o + H')|k\rangle = E_k|k\rangle, \qquad (4.2.2)$$

leads us to the secular determinant

$$\begin{vmatrix} H_{11}-E_k & H_{12} \\ H_{21} & H_{22}-E_k \end{vmatrix} = 0. \qquad (4.2.3)$$

The values of the energy E_k are

$$E_k = 1/2[(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2}]. \qquad (4.2.4)$$

So a doubly degenerate level E_m^o splits in two: E_{m1} and E_{m2},

$$E_{m1} = E_o \pm 1/2\ K, \qquad (4.2.5a)$$

$$E_{m2} = E_o \mp 1/2\ K, \qquad (4.2.5b)$$

where

$$E_o = E_m^o + 1/2\ (H_{11} + H_{22}), \qquad (4.1.6a)$$

$$\Delta = H_{11} - H_{22}, \qquad (4.2.6b)$$

$$K = \sqrt{\Delta^2 + 4|H_{12}|^2} = E_{m1} - E_{m2}. \qquad (4.2.6c)$$

The upper sign in (4.2.5a,b) is taken when $\Delta > 0$, and the lower when $\Delta < 0$. The corresponding coefficients of the eigenstates (4.2.1) are

$$c_{11} = -c_{22} = \sqrt{(K + |\Delta|)/2K} = a, \qquad (4.2.7a)$$

$$c_{12} = c_{21} = \sqrt{(K - |\Delta|)/2K} = b. \tag{4.2.7b}$$

The respective wavefunctions become:

$$|1\rangle = a|1^o\rangle \pm b|2^o\rangle, \tag{4.2.8a}$$

$$|2\rangle = b|1^o\rangle \mp a|2^o\rangle. \tag{4.2.8b}$$

From (4.2.6b,c) we see that Δ is the separation between the unperturbed levels and K the separation between the perturbed ones.

It follows from (4.2.8a,b) that the matrix elements

$$H_{12} = \langle 1^o | H' | 2^o\rangle, \tag{4.2.9}$$

determine to what extent the eigefunctions $|1\rangle$, $|1^o\rangle$ and $|2\rangle$, $|2^o\rangle$ differ from one another. H′ includes the sum of anharmonic terms (cubic, quartic, etc.) of the potential energy and also the deviation of the kinetic energy operator from the form it has in the zero order approximation, although this is usually negligible. There are some interesting considerations from the symmetry point of view concerning (4.2.9). The potential energy of the molecule is invariant under any symmetry operation belonging to its point group, i.e., the operator H′ is totally symmetric. Hence it follows that $|1^o\rangle$ and $|2^o\rangle$ should belong to the same symmetry class, otherwise H_{12} is zero. Thus we have the important rule that in FR only vibrational levels of the same species can perturb one another. This rule restricts severely the limits of the occurrence of resonance interaction in symmetrical polyatomic molecules.

It is interesting to consider the example in which $\omega_1 \approx 2\omega_2$. The observed frequency difference $\omega_1 - 2\omega_2$ will be determined by Δ and $|H_{12}|$. The two extreme cases are:

(a) Sharp resonance, $\omega_1 \approx 2\omega_2$. Thus $\Delta^2 << |H_{12}|^2$, and taking into account that $(1 + x)^{1/2} \simeq 1 + \frac{1}{2}x$ if $x \rightarrow 0$, we have from (4.2.6c)

$$K \simeq 2|H_{12}| \, (1 + \Delta^2/8|H_{12}|^2), \qquad (4.2.10)$$

and the wavefunctions $|1\rangle$ and $|2\rangle$ become

$$|1\rangle = 2^{-1/2}(|1^o\rangle + |2^o\rangle), \qquad (4.2.11a)$$

$$|2\rangle = 2^{-1/2}(|1^o\rangle - |2^o\rangle). \qquad (4.2.11b)$$

(b) The opposite extreme occurs if $\Delta^2 >> |H_{12}|^2$. Here

$$K \simeq \Delta(1 + 2|H_{12}|^2/\Delta^2). \qquad (4.2.12)$$

and the wavefunctions reduce to the unperturbed functions $|1^o\rangle$ and $|2^o\rangle$.

The relationship between $|H_{12}|^2$ and Δ^2 determines the displacement of the levels and the mixing of the wavefunctions, but they may remain insignificant even for a very small Δ, provided that the corresponding anharmonicity constant k in $H' = 1/2\, kQ_1Q_2^2$ is small. This point is important at the time of interpretation of the observed spectra.

A direct consequence of some accidental degeneracy is a redistribution in the intensities between the affected bands. Let us consider the wavefunctions

$$|1\rangle = a|1_p^o\rangle \pm b|2_q^o\rangle, \qquad (4.2.13a)$$

$$|2\rangle = b|1_p^o\rangle \mp a|2_q^o\rangle, \qquad (4.2.13b)$$

where $|1_p^o\rangle$ is a normal mode associated to a fundamental transition and $|2_q^o\rangle$ is an abbreviated form of an overtone or a combination band. The VROA transitions associated with these states are

$$\langle 0|\alpha_{\alpha\beta}|1\rangle\langle 1|T_{\alpha\beta}|0\rangle = a^2\langle 0|\alpha_{\alpha\beta}|1_p^o\rangle\langle 1_p^o|T_{\alpha\beta}|0\rangle$$

$$+ b^2\langle 0|\alpha_{\alpha\beta}|2_q^o\rangle\langle 2_q^o|T_{\alpha\beta}|0\rangle \pm ab(\langle 0|\alpha_{\alpha\beta}|1_p^o\rangle\langle 2_q^o|T_{\alpha\beta}|0\rangle$$

$$+\langle 0|\alpha_{\alpha\beta}|2_q^o\rangle\langle 1_p^o|T_{\alpha\beta}|0\rangle), \qquad (4.2.14a)$$

and

$$\langle 0|\alpha_{\alpha\beta}|2\rangle\langle 2|T_{\alpha\beta}|0\rangle = b^2\langle 0|\alpha_{\alpha\beta}|1_p^o\rangle\langle 1_p^o|T_{\alpha\beta}|0\rangle$$

$$+ a^2\langle 0|\alpha_{\alpha\beta}|2_q^o\rangle\langle 2_q^o|T_{\alpha\beta}|0\rangle \mp ab(\langle 0|\alpha_{\alpha\beta}|1_p^o\rangle\langle 2_q^o|T_{\alpha\beta}|0\rangle$$

$$+ \langle 0|\alpha_{\alpha\beta}|2_q^o\rangle\langle 1_p^o|T_{\alpha\beta}|0\rangle). \qquad (4.2.14b)$$

Then the VROA in the split levels are due to a fundamental transition, an overtone (or combination band) and to a mix of states. The importance of each combination depends on the relatives values of a and b. If (4.2.14) are summed in each case we obtain

$$\langle 0|\alpha_{\alpha\beta}|1\rangle\langle 1|T_{\alpha\beta}|0\rangle + \langle 0|\alpha_{\alpha\beta}|2\rangle\langle 2|T_{\alpha\beta}|0\rangle =$$

$$\langle 0|\alpha_{\alpha\beta}|1_p^o\rangle\langle 1_p^o|T_{\alpha\beta}|0\rangle + \langle 0|\alpha_{\alpha\beta}|2_q^o\rangle\langle 2_q^o|T_{\alpha\beta}|0\rangle. \qquad (4.2.15)$$

This shows that in VROA, as in the Raman spectrum, there is a redistribution in intensities such that the total intensities of the coupled lines is equal to the sum of the respectives line intensities in the unperturbed case.

The symmetry arguments given above were for symmetric polyatomic molecules. Chiral molecules have not this restriction (except in cases of groups C_n and D_n), so FR will be allowed in all cases of accidental degeneracy. Because of the redistribution in the intensities new couplets will appear whose interpretation must rest in (4.2.14a,b). FR of tyrosine and related componds (McHale, 1982) would provide a good example in the doublet at about 830 and 850 cm^{-1}.

4.3 A correlation rule for VROA.

Within the valence optical approach it is assumed that the only internal coordinate which changes the electronic structure of a bond is the stretch of that bond. This enables us to write the derivative of the polarizability with respect to the normal vibrational coordinate Q_p as in eqs. (3.1.8). This is the special case in which the bonds have C_{3v} symmetry or higher. In this kind of molecule the contributions of $\alpha_{\alpha\beta}G'_{\alpha\beta}$ and $(\omega/3)\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}$ are the same in the CID parameter, and $\alpha_{\alpha\alpha}G'_{\beta\beta}$ is zero. The quotient between the polarized and depolarized CID parameter is for 90° scattering,

$$\frac{\Delta_x(90^\circ)}{\Delta_z(90^\circ)} = \frac{4(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})}{7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}} . \tag{4.3.1}$$

Using the definitions given in (2.3.14a-d) we can write (4.3.1) in terms of invariant parameters so,

$$\frac{\Delta_x(90^\circ)}{\Delta_z(90^\circ)} = \frac{12\beta^2(\alpha)}{7\beta^2(\alpha) + 45\alpha^2} = \frac{4\rho}{1+\rho} . \tag{4.3.2}$$

The values of $\beta^2(\alpha)$ and α^2 are always positive, so eq. (4.3.2) establishes the relative values between the vibrational CID spectra polarized and depolarized, where both have the same sign in all bands. In a pure bending vibration the isotropic polarizability is zero, $\alpha = 0$, and from (4.3.2) we have a fixed relation in both classes of bands

$$\frac{\Delta_x(90^\circ)}{\Delta_z(90^\circ)} = \frac{12}{7} = 1.71 . \tag{4.3.3}$$

Within the same restrictions for the axiality of the bonds of any molecule we can obtain from (3.1.8) another expression similar to (4.3.2),

$$\frac{I_x^R - I_x^L}{I_z^R - I_z^L} = 2. \tag{4.3.4}$$

This equation does not involve the degree of polarization of each band, that is, the quotient of the intensity for each related band in the polarized and depolarized spectrum is independent of its degree of polarization.

Hug and Surbeck (1982) have found in (-)-R-3-methylindane the same sign in a polarized and depolarized spectrum covering the region from 200 to 2300 cm^{-1}. This molecule posesses a carbonyl group, that is, it is not in agreement with the original conditions in which eq. (4.3.1) has been developed, but the results indicate a near approximation. As a consequence we can infer that the contribution of the intrinsic optical activity terms are not going to affect the numerator of Δ_x or Δ_z too much, and we can expect a relation nearly equal for molecules with non-axially symmetric bonds. Nevertheless we think that this is not, possibly, the case for molecules with highly polarizable groups. The validity of (4.3.2), within the restrictions in which it is derived, will be of a great support for the bond-polarizability model in VROA, since no extra experimental or computed data (as a molecular force field and bond polarizability parameters) is required. The most important requirement is to possess a good polarized-VROA spectrum free from artifacts.

Special mention must be made to the fact that the relationship (4.3.4) has been found experimentally in resonance experiments of magnetic ROA of ferrocytocrome-C (Barron, Meehan and Vrbancich, 1982).

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PART II

The second part is devoted to VROA calculations and in order to get them it is necessary to firstly perform a vibrational analysis of the molecule and to obtain the bond polarizability parameters of all bonds in question. For the sake of clarity, we shall give all data to reproduce these calculations. These are: molecular geometry (in terms of cartesian coordinates), definition of internal coordinate, molecular force field and bond polarizability data. The G and B matrices have been obtained using the GMAT computer program and the L and L^{-1} matrices thanks to GVIB vibrational analysis program from which the potential enregy distribution of each normal mode can also be calculated . The VROA calculations have been processed in a computer program (B.P. Clark, Ph.D. Thesis, Glasgow University, 1982) although a slight modification was required in order to agree with equations (3.2.13a,d). The experimental details concerning the VROA spectra from the spectrometer in Glasgow are well described elsewhere (Barron, L.D. and Vrbancich, J. in "Topics in Current Chemistry", Vol. 123, ed. F.L. Boschke, Springer, Berlin, Heideberg, 1984). The spectra have been taken from the literature and the infrared frequencies of the molecules in Chapters 7 and 8 have been measured on a Perkin-Elmer 580 spectrometer by the infrared service at this department. The results are of similar accuracy to those in the Raman case.

5 (R)-(+)-BROMOCHLOROFLUOROMETHANE

This molecule is a good example for application of the bond polarizability theory of VROA. A vibrational analysis has been carried out (Diem and Burow, 1975) so we know the force field. This consideration together with the fact that all the bonds are axially symmetric, for which electro-optic parameters are available (Sverdlov et al., 1974; Holzer, 1968; Weber, 1955). The unique problem concerning this molecule is that it is very difficult to resolve the racemic mixture and no VROA spectra have been obtained so far. Several theoretical studies have been developed in infrared (Marcott et al., 1977) and Raman (Prasad and Burow, 1979; Prasad and Nafie, 1979) optical activity. The last one uses the atom-dipole interaction model to calculate the CID. Barron and Clark (1982) have used the bond polarizability theory to calculate the VROA spectrum of this molecule. Some computational mistakes have made it advisable to calculate the CID spectrum again within the same theory .

Table 5.I.- Principal cartesian cordinates of CBrClFH.

atom	x/A	y/A	z/A
H	-1.5565	0.5928	0.7215
C	-0.4362	0.4531	0.6393
Br	0.0216	-0.1613	-1.1283
Cl	0.0581	-0.6952	1.8681
F	0.1603	1.6403	0.8651

The fig. (5.1) is an ORTEP diagram of the bromochlorofluoromethane based on the cartesian cordinates given in table 5.I. Barron and Clark's (1982) definition of internal coordinates were used as well as the electro-optic parameters (table 5.II).

Table 5.II.- Bond-polarizability data for CBrClFH.

bond	Δ/A^3	α'/A^2	Δ'/A^2
C-H	0.20	1.08	2.13
C-Br	3.40	2.07	2.40
C-Cl	2.10	2.00	2.14
C-F	0.80	1.00	2.00

These values can be converted into SI units by multiplying the factor a $CV^{-1}m^2/A^3$ in Δ and a' $CV^{-1}m$ $/A^2$ in Δ' and α', where $a = 1.11265\ 10^{-40}$. $a' = 10^{-8} a$.

The valence force constants have been displayed in table 5.III. We show directly the atom involved in a particular internal coordinate rather than the notation followed in the original work. It must be pointed out that this valence force field corresponds to the gas-phase of the HCBrClF although no VROA spectra have been published for a gas.

Our vibrational results match with those previously calculated in frequency and in potential energy distribution of each normal mode. The results obtained are displayed in table 5.IV. The calculated polarized and depolarized CID spectra are shown in the last two columns. The values between brackets correspond to those calculated within the atom dipole interaction model (ADI). We observe that the agreement in sign between both theories is rather poor and the values of the ADI-model are, in general, one order of magnitude higher than the

Table 5.III.- Valence force constants for CBrClFH.

f. c. n°	atomos involved	values
Stretching		
1	C-Cl	3.45038
2	C-F	5.18040
3	C-H	5.00099
4	C-Br	2.48255
Bending		
5	Cl-C-F	1.38660
6	Cl-C-H	0.80486
7	Cl-C-Br	1.33426
8	H-C-F	0.75714
9	Br-C-F	1.36610
10	Br-C-H	0.61788
Stretch-Stretch		
11	C-Cl, C-F	0.84588
12	C-Cl, C-Br	0.74570
13	C-Br, C-F	1.07762
Stretch-Bend		
14	C-Cl, Cl-C-F	0.59060
15	C-Cl, Cl-C-H	0.26149
16	C-F , H-C-F	0.51796
17	C-H , Br-C-H	-0.25375
18	C-Br, Cl-C-Br	0.25630
19	C-Br, Br-C-H	0.09380
Bend-Bend		
20	Cl-C-Br, Cl-C-F	0.21120
21	Br-C-H , H-C-F	0.02071

The units are mdyn A^{-1} for stretching and stretch-stretch interactions; mdyn rad^{-1} for stretch-bend; and mdyn A rad^{-2} for bending and bend-bend interactions.

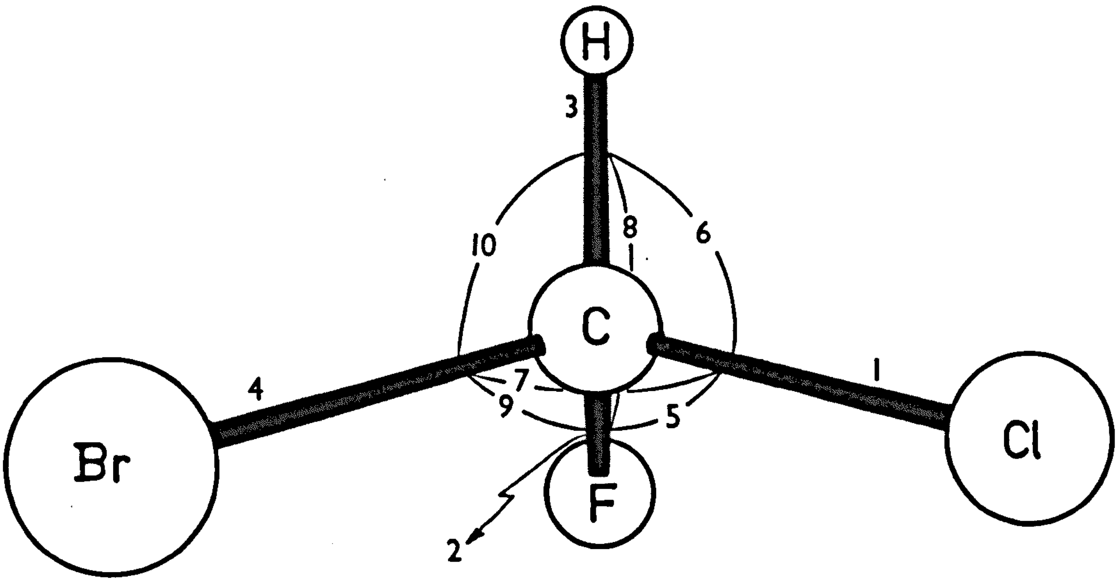

Figure 5.1.- Definition of the internal coordinates in the (R)-(+)-bromochlorofluoromethane.

bond-polarizability model. The first band (3026 cm^{-1}) is particulary interesting. We have shown elsewhere (Section 4.3) that, independently of the force fields and electro-optic parameters, if a molecule has all its bonds axially symmetric its polarized and depolarized spectrum have the same sign in all bands. The calculated Δ_x and Δ_z depend strongly on the intermediate data but an experimental proof of a polarized and depolarized spectrum of the same molecule (provided that all its bonds are axially symmetric) will decide the best theoretical interpretation.

Table 5.IV.- Calculated CID parameters Δ_x and Δ_z using the bond polarizability model. The values between brackets correspond to the atom dipole interaction model (Prasad and Nafie, 1979).

	Frequencies			
Normal mode	Obs.(*) /cm^{-1}	Cal. /cm^{-1}	POLARIZED $x/10^{-4}$	DEPOLARIZED $z/10^{-4}$
1	3026	3039	-0.01 (-0.08)	-0.03 (0.46)
2	1131	1302	1.48 (-5.16)	1.02 (-8.16)
3	1205	1203	-0.62 (3.01)	-0.79 (5.77)
4	1078	1074	-0.16 (0.35)	-0.16 (0.88)
5	788	794	0.58 (-2.10)	1.27 (-1.41)
6	664	670	-0.22 (-1.90)	-0.67 (-2.25)
7	427	425	0.44 (-7.67)	0.29 (-10.9)
8	315	310	0.61 (7.64)	0.37 (34.3)
9	226	224	-5.36 (-6.16)	-0.34 (-4.74)

(*) Frequencies corresponding to the gas-phase.

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6 (S)-(-)-EPOXYPROPANE

The second molecule for which we shall compute the CID spectrum of VROA is (S)-(-)-epoxypropane. This molecule is particularly interesting because its spectrum is available (Barron and Vrabancich, 1983), a force field has been attempted (Polavarapu and Michalska, 1984) and all its bonds are axially symmetric. These reasons make it, in principle, a perfect example to be studied.

The cartesian coordinates of this molecule have been displayed in Table 6.I. With those coordinates the pictures of Fig 6.1 have been drawn. Fig 6.1a represents the definition of the internal coordinates , and Fig 6.1b shows the numeration of the internal coordinates (i.c.) as well as the numeration of the atoms. The numeration of the stretching coordinates and the bonds is the same. In the notation and definition of the i.c. we follow Polavarapu and Michalska (1984).

Unfortunately the polarized VROA spectrum of this molecule has not been obtained, as this would be ideal for testing the ideas outlined in Section 4.3. It is a small chiral molecule, well resolved and its force field is reasonably known. It is the hope that in the future the (S)-(-)-epoxypropane would determine the validity of the bond polarizability theory applied to VROA.

Table 6.I.- Equilibrium cartesian coordinates of (S)-(-)-epoxypropane.

Atom	x/A	y/A	z/A
C(1)	0.7350	0.0000	0.0000
C(2)	-0.7350	0.0000	0.0000
O(3)	0.0000	1.2330	0.0000
C(4)	1.4754	-0.2968	1.2856
H(5)	1.2645	-0.2123	-0.9194
H(6)	-1.2645	-0.2123	0.9194
H(7)	-1.2645	-0.2123	-0.9194
H(8)	0.8427	-0.0432	2.1362
H(9)	1.7274	-1.3566	1.3234
H(10)	2.3896	0.2955	1.3234

The bond polarizability parameters, listed in Table 6.II, are taken from Barron and Clark (1982). The transferability of the electro-optical parameters (e.o.p) assumes similar bonds from not very different molecules. In this case no bond-polarizability derivatives of ethers have been published, for this reason the C_α-H e.o.p comes from acetone, and the C-O from the carbonyl group, >C=O, in acetone modified by a factor of 1/2. Several calculations have been run for different factors (|factor|<1) and they do not affect the signs of Δ_z. The C-C bonds correspond to saturated alkanes, the rest belong to a methyl group.

Table 6.III gives the valence force field of this molecule. These have been obtained from ethylene oxide and the methyl group from the acetaldehyde but this table does not follow exactly all the force constants (f.c.) from the original paper. Some of them have been redefined in order to make a comprehensible interpretation of the relationship f.c.-i.c. (Polavarapu, private communication). The f.c. not listed are taken to be zero.

Table 6.II.- Bond polarizability data for epoxypropane.

Bond no.	$/A^3$	$'/A^2$	$'/A^2$
1	0.11	1.25	1.13
2	0.18	2.78	0.99
3	0.11	1.25	1.13
4	0.11	1.25	1.13
5	0.05	1.46	0.92
6	0.60	1.40	0.92
7	0.60	1.40	0.92
8	0.11	2.04	0.92
9	0.11	2.04	0.92
10	0.11	2.04	0.92

(The units are the same as in Table 5.III)

The calculated and observed Δ_z values are in Table 6.IV, together with the calculated and observed frequencies (infrared and Raman). An assignment of these frequencies is made elsewhere (Durig, Nease and Rizzolo; 1982). As we can see in the spectrum (fig. 6.2) the ratio signal/noise make imposible the assigment of the sign to some bands (1499 and ~214 cm^{-1}) . The correlation, in our opinion, is good considering the approximate data we have used in order to calculate the Raman intensities and the CIDs for each band. The values of Δ_x are not reported because its VROA polarized spectrum is not recorded.

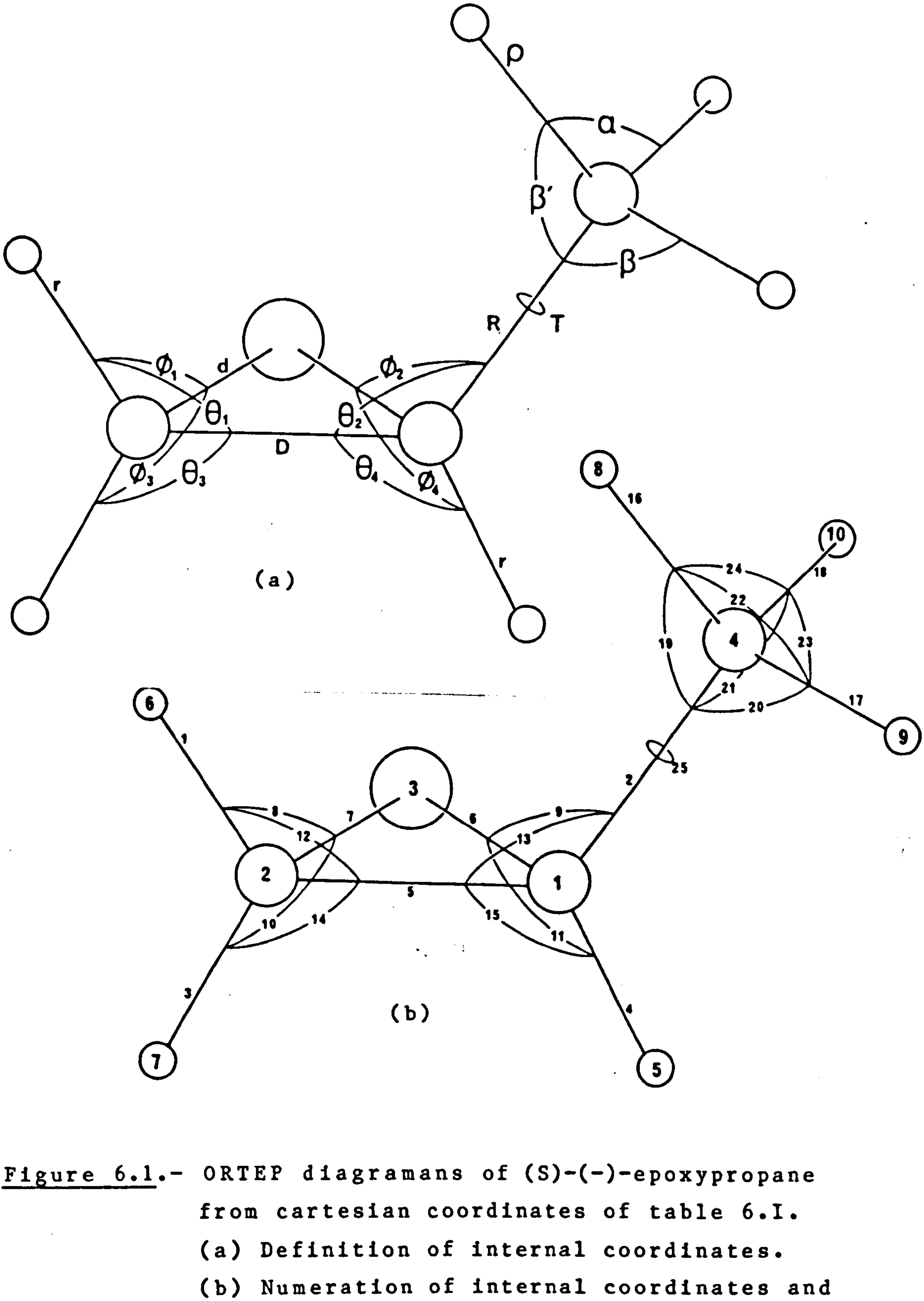

Figure 6.1.- ORTEP diagramans of (S)-(-)-epoxypropane from cartesian coordinates of table 6.I.
(a) Definition of internal coordinates.
(b) Numeration of internal coordinates and atoms.

Table 6.III.- Valence force constants for epoxypropane.

Stretching			
f_r	5.01	f_d	4.54
f_D	4.52	f_R	4.08
f_ℓ	4.88		
Bending			
$f_{\phi 1}$	0.81	$f_{\phi 2}$	0.78
$f_{\phi 3}$	0.81	$f_{\phi 4}$	1.01
$f_{\theta 1}$	0.87	$f_{\theta 2}$	0.89
$f_{\theta 3}$	0.87	$f_{\theta 4}$	1.08
f_β	0.45	$f_{\beta'}$	0.49
f_α	0.45		
Stretch-Stretch			
f_{dd}	0.55	f_{dD}	-0.24
$f_{rr}=f_{Rr}$	0.08	f_{Rr}^{cis}	0.05
$f_{rr}^{tr}=f_{Rr}^{tr}$	-0.03	$f_{\ell\ell}$	0.07
Stretch-Bend			
$f_{D\phi}$	-0.07	$f_{D\theta}$	0.43
$f'_{d\phi}$	-0.08	$f'_{d\theta}$	0.06
$f_{d\phi}$	0.20	$f_{d\theta}$	-0.22
$f_{R\beta}$	-0.02		
Bend-Bend			
$f_{\phi 1\theta 1,\phi 3\theta 3}$	-0.26	$f_{\phi 2\theta 2}$	-0.14
$f_{\phi 4\theta 4}$	-0.38	$f_{\phi 1\phi 3}$	0.08
$f_{\phi 2\phi 4}$	-0.24	$f_{\theta 1\theta 3}$	0.20
$f_{\theta 2\theta 4}$	0.21	$f_{\phi 1\theta 3,\phi 3\theta 1}$	0.14
$f_{\phi 2\theta 4}$	0.55	$f_{\phi 4\theta 2}$	0.31
$f_{\phi 1\phi 2}$	-0.04	$f_{\phi 3\phi 4}$	-0.03
$f_{\theta 1\theta 2}$	-0.02	$f_{\theta 3\theta 4}$	0.06
$f_{\phi\phi}^{tr}$	-0.01	$f_{\phi\theta}^{cis}$	-0.05
$f_{\phi\theta}^{tr}$	-0.01	$f_{\theta\theta}^{tr}$	0.08
$f_{\beta\beta'}$	-0.02		
Torsion			
f_τ	0.006		

All units are in mdyn A^{-1}.

Table 6.IV.- Correlation between theoretical (experimental) frequencies and Δ_z.

Cal. freq.	Obser. freq.		Cal. $\Delta_z/10^{-4}$	Obs. Δ_z (sign)
	ir	Raman		
1514	1498	1499	0.04	?
1478	1472		0.41	
1452	1456		-0.12	
1449	1477	1453	-0.68	+
1394	1403	1395	0.61	-
1334	1369	1363	-0.58	+
1241	1265	1260	-1.13	-
1162	1167	1163	0.67	-
1139	1143	1135	0.53	+
1064	1103	1100	-0.30	-
1019	1023	1019	1.60	+
957	950	944	3.12	+
899	895	891	-0.29	-
828	829	826	1.58	-
732	746	731	2.41	+
432		~411	-1.67	-
368		~373	-1.27	-
123		~214	-0.63	?

The frequencies are given in cm^{-1}.

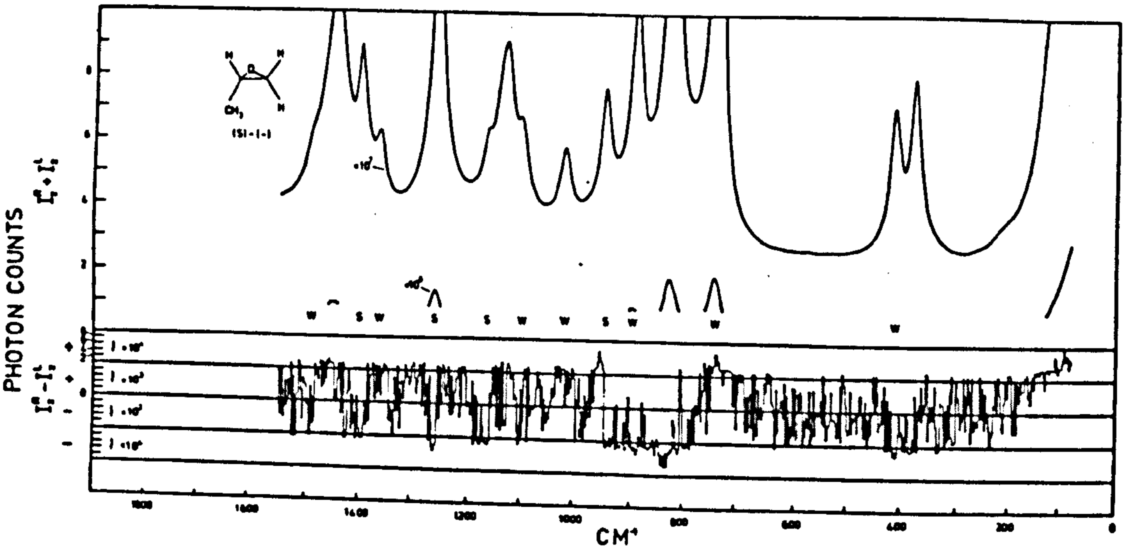

Figure 6.2.- Raman and VROA spectra of (S)-(-)-epoxypropane (Barron and Vrbancich,1983).

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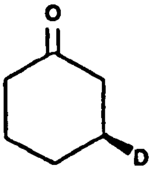
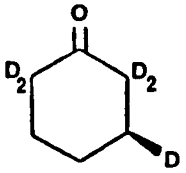
7 VROA OF SOME DEUTERATED CYCLOHEXANONES

This chapter is concerned with the study of two deuteraed cyclohexanones: (3S)-(+)-deuterocyclohexanone (I), and (3S)-(+)-2,2,3,6,6-pentadeuterocyclohexanone (II),



(I)

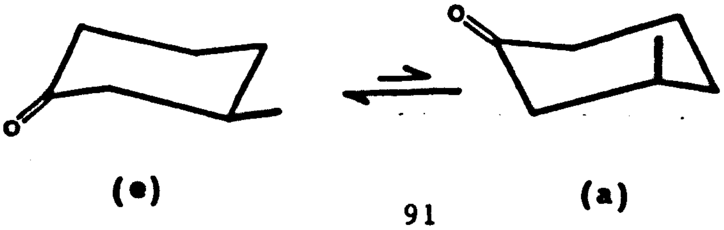


(II)

The VROA spectra of these two molecules are available (Torrance, 1983) and a qualitative interpretation has been attempted in the same source. Fuhrer et al. (1972) have made an exahustive vibrational analysis of the cyclohexanone and several symmetrical deuterated analogues. We shall use the force field and the geometry proposed there in the study of the VROA spectra of (I) and (II).

7.1 Stereochemistry.

It is well established that the chair conformation of the cyclohexanone is the most favoured (Tai and Allinger, 1966). The molecules (I) and (II), with the chiral deuterium substituted at C_3, will exist in two chair conformations in practically the same ratio (1:1). The axial position of the deuterium has, rigorously speaking, less steric effect than the equatorial (Barth and Djerassi, 1981) but there is not much difference. The equilibrium is



(7.1.A)

Here we have omitted the intermediate boat configuration. As a consequence a solution of (I) or (II) contains the equatorial and axial conformation.

7.2 The normal coordinate analysis.

Molecules (I) and (II) are isotopomers of the cyclohexanone and in our calculations we have followed the notation of the internal coordinates (i.c.) and the force field (f.f.) of Fuhrer et al. (1972), as well as the numerical representation of the i.c. . The vibrational programs and the data input have been checked for the case of the cyclohexanone and the results (frequencies and potential energy distribution -PED-) agree with those given in the original reference. The calculated normal mode frequencies together with the experimental ones (infrared and Raman) are displayed in table 7.IIIa for (I) and table 7.IIIb for (II). The reasons given above makes it necessary to calculate both axial and equatorial conformations. Both tables show a close agreement between experimental and calculated frequencies. No attempt of further refinement to the force field was made. The most important results, from the normal coordinate analysis, are the $\underset{\sim}{s}$-vector and $\underset{\sim}{L}$ and $\underset{\sim}{L}^{-1}$ matrices, which are obtained routinely and used afterwards as an input in the VROA calulations.

7.3 The bond polarizability data.

These are shown in table 7.I. The paraneters required are Δ_i, Δ'_i, α'_i. The values were taken in the assumption of the transferability of the electro-optic parameters. Bonds C=O, C_1-$C_{2,6}$ and $C_{2,6}$-H comes from acetone (Vakhlyueva et al., 1967), the others from the cyclohexanone (Gussoni et al., 1977). The isotropic bond polarizabilities and polarizability anisotropies are from Le Fèbre (1965). We have assumed in our calculations that the carbonyl bond is axially symmetric which means that the anisotropic polarizabilities $\alpha^1 = \alpha_{\parallel} - \alpha_{\perp}^1$, $\alpha^2 = \alpha_{\parallel} - \alpha_{\perp}^2$ are equal. If different values of the anisotropies are used (Vakhlyueva et al., 1967) the calculated signs are not affected. Anyhow, inclusion of the C_{2v} symmetry of the carbonyl group would require the formulation given in Section 3.3 and just a test of including $\alpha^1 = \alpha^2$ in the calculations is not enough to conclude the small influence of the C_{2v} anisotropy within the VROA (Barron and Clark, 1982).

Table 7.I .- Bond polarizability data for the deuterated cyclohexanone (I) and (II).

	Δ / A^3	Δ' / A^2	α' / A^2
C=O	1.20	2.80	1.83
$C_1-C_{2,6}$	1.80	2.78	0.99
C-C	0.05	1.46	0.92
$C_{2,6}-H$	0.11	1.25	1.13
C-H	0.32	2.20	1.30

For SI units see table 5.II.

7.4 VROA calculations.

The calculated and experimental VROA features are shown in tables 7.IIIa,b with the corresponding frequencies for molecules (I) and (II) in equatorial and axial positions. The CID calculated parameter, Δ_z, in the case of two near calculated frequencies which are assigned to a single experimental band is

$$\Delta = [a\ \mathrm{num}(\Delta^a) + e\ \mathrm{num}(\Delta^e)]/[a\ \mathrm{den}(\Delta^a) + e\ \mathrm{den}(\Delta^e)], \qquad (7.4.1)$$

where "num" and "den" means numerator and denominator, e and a represent the mole fractions of each species. We shall comment on the most important characteristic of the spectrum.

7.4.1. Vibrational normal modes involving the carbonyl group.

The internal coordinates associated with the carbonyl group are (see fig. 8.1): the stretch (ν), two in plane bends (ϵ) and the out of plane bend (ρ). In table 7.II is presented the main frequencies and VROA signs corresponding to those i.c..

Table 7.II.- Main frequencies of the carbonyl group.

	stretch		out of plane		in plane	
	calc.	obs.	calc.	obs.	calc.	obs.
(I)e	1715(+)	1715(?)	636(+)	642(?)	477(+)	492(-)
(I)a	1715(+)		632(+)		484(+)	
(II)e	1709(+)	1709(+)	611(+)	612(?)	460(+)	454(?)
(II)a	1709(+)		609(+)		462(+)	

Units of frequencies in cm^{-1}. e and a mean equatorial and axial conformers.

The calculations show a definite positive CID sign in all bands for the different positions of the deuterium (equatorial or axial).

Stretch.-

In (I) is well established at 1715 cm^{-1} but the experimental assigment of the CID sign is ambiguous.

In (II) there is a good correlation between both, calculated and experimental values and sign.

Out of plane.-

In (I) can be assigned to 642 cm^{-1} because the calculated are 636 cm^{-1} (equatorial) and 632 cm^{-1} (axial), with a PED associated with the out of plane i.c. of 34 and 36%. As we can see in the spectrum (fig. 7.1a) the CID was not recorded in this zone because of artifacts.

In (II) the out of plane frequency is established at 612 cm^{-1} and the calculated are 611 (equatorial) and 609 cm^{-1} (axial) with a PED of 26 and 29% in that i.c.. As in the above case no CID sign can be extracted from the spectrum (fig. 7.1b).

In plane.-

In (I) the band centered at 492 cm^{-1} seems to contains the in plane frequency of the equatorial and axial deuterium at the calculated positions of 484 and 477 cm^{-1} with a PED of 50 and 52% each one in this i.c.. The experimental sign seems to be negative at 492 cm^{-1} although the calculated values are positive for all the frequencies associated with the in plane frequency.

In (II) the frequency of the strong band at 454 cm^{-1} corresponds to the in plane frequency because the calculated ones associated with this internal coordinate are 460 (equatorial) and 462 cm^{-1} (axial)with 51 and 54% of PED in this internal coordinate. The shoulder at 440 cm^{-1} could be related to the calculated frequencies at 466 (equatorial) and 439 cm^{-1} (axial) which correspond to skeletal bending.

7.4.2 Bending vibrations of methylene groups.

This is the zone between 1700 and 700 cm^{-1}. The region 1500 - 1400 cm^{-1} is assigned to CH_2 scissoring as group frequency in both compounds (I) and (II). The VROA feature is not well established and only at the frequency 1467 cm^{-1} agrees with the calculated values; in other cases either the CID spectrum presents too many fluctuations inside the noise zone or no complete agreement is obtained with the calculated signs.

Below 1400 cm^{-1} we have just delocalized frequencies corresponding to <HCH and <CCH deformation bands together with mainly C-C stretchings. The CID spectra seem to be richer in this area. No good correlation appears between calculated and experimental Δ_z. The broad negative band around 1200 cm^{-1} in the CID spectra of both but no special insight can be extracted from the PED when we correlate both bands. At 923 cm^{-1} for (I) and at 907 cm^{-1} for (II) appears another broad and negative CID band, and as above no special assignment localized in a group of i.c. is possible because the PED is spread.

Table 7.IIIa.- (3S)-(+)-deuterocyclohexanone, (I).

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Raman	cal.	obs.
1715	1715	1713	1715	0.81	?
		1628			
1465	1465	1465	1467	-0.43	-2.5
1448	1448	1458	1454	-1.73	?
1430	1430	1449		8.50	
		1442			
1382				4.81	
	1373			1.66	
1344		1348	1348	0.50	?
	1343	1344		-2.32	
1333		1338		-2.55	
	1319			-0.27	
1314	1312	1314	1318	1.52	3.5
1294	1296	1303	1307	0.16	?
	1276	1281	1282	1.46	5.3
			1272		5.3
1263		1262		-1.48	
	1247	1252	1252	5.02	4.8
1252		1250		-1.73	
1234	1233	1223	1226	0.66	-2.2
1212			1212	0.11	-3.4
1196	1200	1201		0.11	
	1193			4.96	
		1172	1176		-2.8
	1149			-1.38	
1112				-1.70	
1108		1103	1107	-2.52	5.7
1091	1094		1095	2.13	9.0
	1088	1087		-3.03	
1060		1064	1070	-2.53	5.3
	1044	1050	1041	-2.14	3.4

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta_z/10^{-4}$	
equ.	axi.	IR	Raman	cal.	obs.
		1037			
		1020	1023		4.3
		992	993		?
		982	988		?
952	961	944	947	3.95	3.1
	939			5.82	
918		921	923 w	-0.34	17.7
	892	900	903	0.95	10.6
877		885	885	2.53	6.7
873			878 w	-0.78	?
	860	857	865 s	7.85	
827		839	842 s	-2.68	
	815	800	801 s	0.40	
770	774	782	784 s	0.49	
		757	750 s		
		747			
737	736	726	733	0.40	
	717			1.44	
685		695	699 s	0.56	
636	632	641	642 s	3.72	
484	484	491	492	2.49	?
477	476	475	478	4.36	-2.5
450				0.07	
	439			0.04	
420		400	406	0.48	3.2
	414	396	397	3.97	-3.2
285	283	303	303	1.67	6.6
193	193		180	3.90	(-)
121	120		103	-0.83	(-)

w and s refer to weak and strongly polarized Raman bands.

Table7.IIIb.- (3S)-(+)-2,2,3,6,6-pentadeutero-cyclohexanone, (II).

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Raman	cal.	obs.
1709	1709	1707	1701	0.90	2.5
1466	1466	1457	1459	0.33	?
1448	1448	1448	1451	-1.90	?
1376	1368	1381		2.37	?
			1352		?
1334	1338	1336	1342	0.30	8.9
1314		1311	1316	-1.74	?
	1301	1297	1301	2.22	?
1294	1293			1.32	
1271	1269	1273	1275	-0.25	?
1224	1231			1.49	
		1209	1215		-2.0
1192	1197			1.58	
		1165	1166		8.3
1145	1149	1143	1149	-3.70	?
	1121	1115	1116	-1.41	?
1101		1105	1108	0.09	?
1090	1083	1086	1089	-2.02	(-)?
		1072	1070		?
1055	1053	1049	1051	-6.67	-2.1
1041	1039			2.47	
1038	1032	1033	1036	1.89	?
1014		1021	1021	2.36	?
		992	993		3.2
		981			
	963	972	974	0.29	4.8
935	944	930	931	4.40	?
	909	905	907	0.23	-4.3
890		891	893	-0.90	-7.3
857	859	849	850	0.56	?

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Raman	cal.	obs.
	848		840	4.05	-7.0
834		823	825	-1.72	-6.3
	793	795		0.83	
783		785	787 s	1.23	
	775		778 s	1.63	
769			771 s	-0.64	
		766	763 s		
	747			2.61	
739				-0.37	
734		736	738 s	1.43	
	720			-4.65	
	697	700	700 s	-1.51	
689		690	692 s	1.41	
	656			-1.85	
		647	650 s		
642				-1.22	
611	609	614	612 s	3.06	
		467			
460	462	453	454	2.35	?
446	439		440	1.55	?
415	403	400		3.64	
		386	387		?
		378	380		?
374	373	355	356	-0.01	?
279	277	300	297	1.13	?
175	176		~170	8.58	?
114	113		~ 93	-0.48	(-)

The infrared and Raman frequencies in tables 7.IIIa,b as well as the spectra contained in Chapter 7 were kindly supplied by Dr. J. F. Torrance (University of Glasgow).

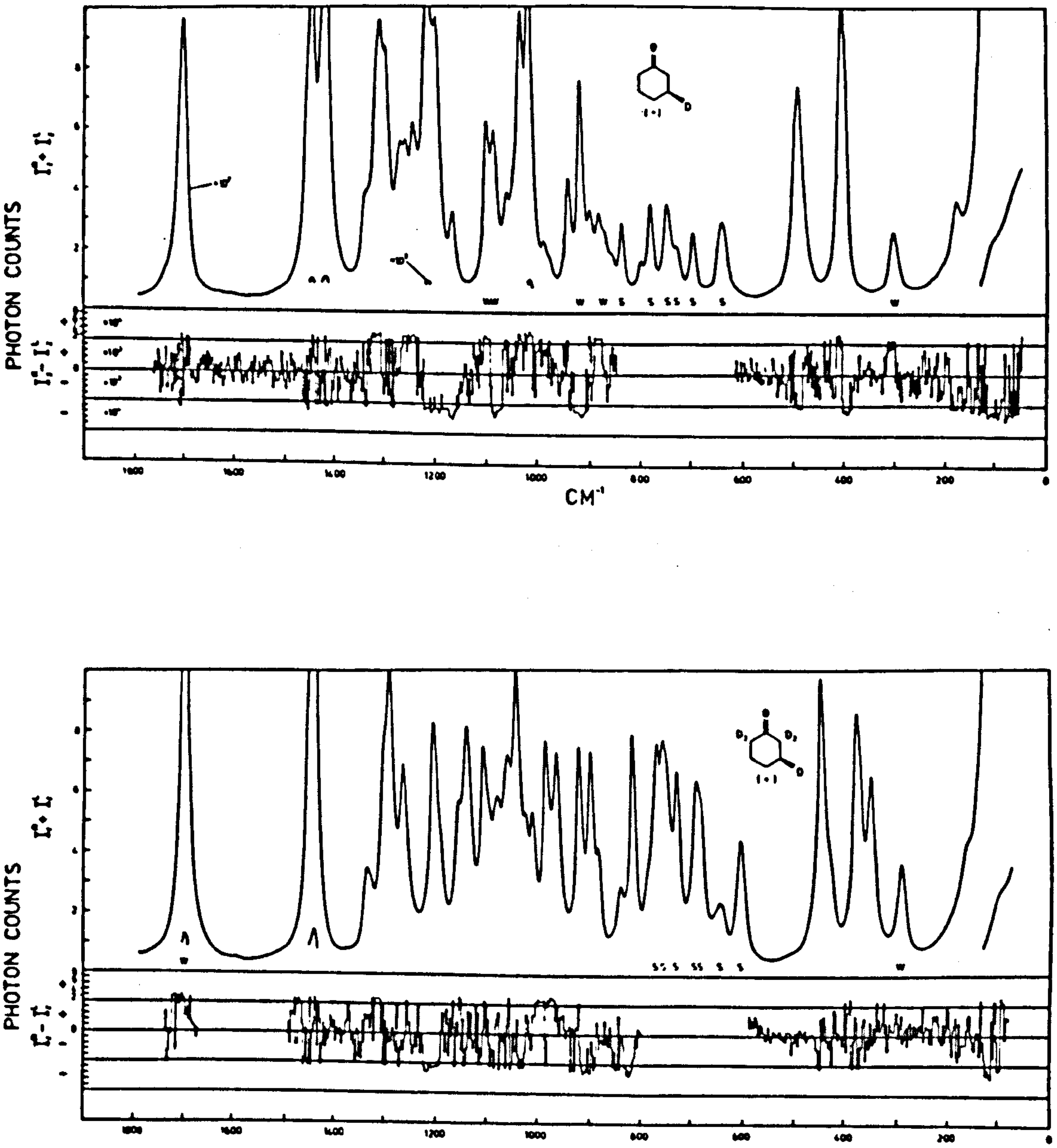


Figure 7.1.- Raman and VROA spectra of (I) and (II), from Torrance (1983).

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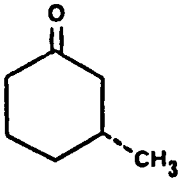
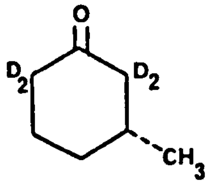
8 VROA OF SOME METHYLATED CYCLOHEXANONES

We shall develop the calculations for the molecules (3R)-(+)-methylcyclohexanone (III), and (3R)-(+)-2,2,6,6-tetradeutero-3-methylcyclohexanone (IV).



(III)



(IV)

Molecule (III) has been the object of much study in VROA. The publication and a first attempt at a qualitative description was carried out by Barron (1978); Polavarapu and Nafie (1980) performed the calculations based on the atom-dipole interaction (ADI) model; Barron and Clark (1982) used the generalized two group model combined with the bond polarizability theory, and Freedman et al. (1984) repeated the calculations using the ADI model improving the force field based on six isotopomers of 3-methylcyclohexanone, including species (III) and (IV); no further attempt at explaining the theoretical CID spectra of the isotopomers therein contained was made because they have not been experimentally recorded up to date. The depolarized CID spectrum of molecule (IV) was recorded on a multichannel instrument, Anaspec-36. Information on ROA multichannel instruments are available from Hug's references. This late case is just a very preliminary spectrum and for this reason has not been included in the context: only the observed signs of each band are presented.

Table 8.I.- Cartesian coordinates for (III) and (IV).

Atom nº	x/A	y/A	z/A
O(1)	0.0	0.0	0.0
C(2)	1.22000	0.0	0.0
C(3)	2.01488	1.27208	0.0
H(4)	2.49096	1.40687	-0.98245
H(5)	1.33959	2.12632	0.15568
C(6)	3.08838	1.26543	1.09017
H(7)	2.60859	1.33512	2.07753
C(8)	3.95460	2.53761	1.03708
H(9)	4.49978	2.60425	0.09557
H(10)	4.68617	2.55036	1.84500
H(11)	3.34301	3.43507	1.12987
C(12)	3.94614	0.0	1.02825
H(13)	4.53286	0.0	0.09778
H(14)	4.66041	0.0	1.86480
C(15)	3.08838	-1.26543	1.09017
H(16)	3.73177	-2.15034	0.97651
H(17)	2.60859	-1.33512	2.07753
C(18)	2.01488	-1.27208	0.0
H(19)	2.49096	-1.40687	-0.98245
H(20)	1.33959	-2.12632	0.15568

8.1 Stereochemistry.

The equilibrium of (7.1.A) will take place with a 70% of the equatorial position of the methyl group, and a 30% in the axial one (Lightner and Crist, 1979). So far in all cases quoted above the VROA calculations were performed in the assumption that the equatorial form was the only one present in the solution. Obviously it is the most stable but we cannot ignore the axial. The methyl group was supposed to be in a staggered position with respect to the ring.

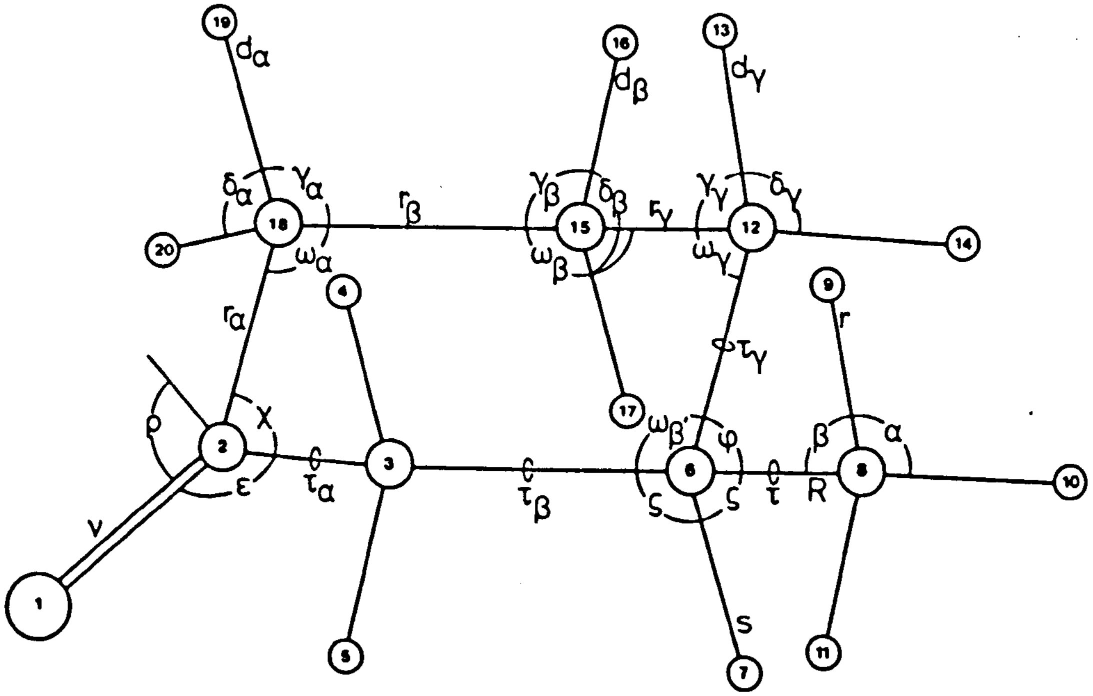


Figure 8.1.- Definition of internal coordinates in (III) and (IV).

8.2 The normal coordinate analysis.

The refinement force field of Freedman et al. (1984) has been adopted in order to develop the normal coordinate analysis of (III). Table 8.II shows the force field, the notation of the internal coordinates corresponds to that of fig. 8.1, which is slightly different from that used by Barron and Clark (1982) in the methyl group. This is done in order to fit with the notation of Snyder and Schachtsneider(1964). The experimental (infrared and Raman) and the calculated frequencies for (III) and (IV) with the methyl group in equatorial and axial positions are displayed in tables 8.III-IV respectively. The cartesian coordinates are shown in table 8.I, where the position of the ring is from Fuhrer et al. (1972) and the methyl group corresponds to a methyl group in the isobutane (Tables of interatomic distances, 1958).

8.3 Bond polarizability data.

Table 6.II contains the bond polarizability data of the methyl group, which together with table 7.I will complete the corresponding data of molecules (III) and (IV). A complete table is given in Barron and Clark's (1982) work and will not be repeated in this section. We make extensive use of the comment on the internal symmetry of the carbonyl group in Section 7.3.

Table 8.II.- Valence force constants used in methylated cyclohexanones.

CYCLOHEXANONE-RING

symbol	coordinates involved	common atoms	value[a]	value[b]
stretch				
K_d^α	C-H		4.685	
K_d^β	C-H		4.610	
K_d^γ	C-H		4.533	
K_ν	C=O		9.652	
K_r^α	C-C		4.564	
K_r^β	C-C		4.186	
K_r^γ	C-C		4.136	
bend				
H_δ^α	<HCC		0.554	
H_δ^β	<HCH		0.567	
H_δ^γ	<HCH		0.579	
H_γ^α	<HCC		0.628	
H_γ^β	<HCC		0.657	
H_γ^γ	<HCC		0.679	
H_ω^α	<CCC		1.068	0.550
H_ω^β	<CCC		1.024	
$H_\omega^{\beta'}$	<CCC		1.024	
H_ω^γ	<CCC		1.024	
H_χ	<CCC		1.111	1.110
H_ϵ	<CCO		0.919	0.936
H_ϱ	<C-CO-C		0.534	0.625
torsion				
H_τ^α	<CC-CC		0.008	0.010
$H_\tau^{\beta,\gamma}$	<CC-CC		0.093	0.170
stretch-stretch				
$F_{\alpha\alpha}$	C-H, C-H	C	0.006	
$F_{r,r}$	C-C, C-C	C	0.101	

symbol	coordinates involved	common atoms	value[a]	value[b]
stretch-bend				
$F_{r,\gamma}$	C-C, <HCC	C-C	0.328	
$F'_{r,\gamma}$	C-C, <HCC	C	0.079	
$F_{r,\omega}$	C-C, <CCC	C-C	0.417	
$F^{\alpha}_{r,\omega}$	C-C, <CCO	C-C	0.417	
$F_{r,\chi}$	C-C, <CCC	C-C	0.417	
bend-bend				
$F_{\gamma\gamma}$	<HCC, <HCC	C-C	-0.021	
$F'_{\gamma\gamma}$	<HCC, <HCC	H-C	0.012	
$F^{t}_{\gamma\gamma}$	<HCC, <HCC (trans)	C-C	0.127	
$F^{g}_{\gamma\gamma}$	<HCC, <HCC (gauche)	C-C	-0.005	
$F_{\gamma\omega}$	<HCC, <CCC	C-C	-0.031	
$F^{t}_{\gamma\omega}$	<HCC, <CCC (trans)	C-C	0.049	
$F^{g}_{\gamma\omega}$	<HCC, <CCC (gauche)	C-C	-0.052	

METHYL-GROUP[c]

symbol	coordinates involved	common atoms	value
stretch			
K_r	C-H		4.699
K_s	C-H		4.588
K_R	C-C		4.387
bend			
H_{α}	<HCH		0.540
H_{β}	<CCH		0.645
H_{γ}	<CCH		0.657
H_{τ}	<CCC		1.084
torsion			
H_{Γ}	<CC-CH		0.024
stretch-stretch			
F_{rr}	C-H, C-H	C	0.043

symbol	coordinates involved	common atoms	value
stretch-bend			
$F_{R_\beta, \zeta}$	C-C, <CCH	C	0.328
$F'_{R_\beta, \zeta}$	C-C, <HCC	C	0.079
$F_{R\phi}$	C-C, <CCC	C	0.417
bend-bend			
$F_{\beta\beta}$	<CCH, <CCH	C-C	-0.012
$F'_{\zeta\zeta}$	<CCH, <CCH	C-H	0.012
$F_{\phi\phi}$	<CCC, <CCC	C-C	-0.041
$F_{\zeta\phi}$	<CCH, <CCC	C-C	-0.031
$f^t_{\zeta\gamma}$	<H1CC, <CCH2 (trans)	C-C	0.127
$f^g_{\zeta\gamma}$	<H1CC, <CCH2 (gauche)	C-C	-0.005
$f'^t_{\zeta\gamma}$	<H2CC, <H1CC1(trans)	C-C	0.002
$f'^g_{\zeta\gamma}$	<H2CC, <H1CC1(gauche)	C-C	0.009
$f^t_{\gamma\phi}$	<H1CC, <CCC1 (trans)	C-C	0.049
$f^g_{\gamma\phi}$	<H1CC, <CCC1 (gauche)	C-C	-0.052

(a) Fuhrer et al. (1972).

(b) Freedman et al. (1984).

(c) Snyder and Schachtschneider (1965).

- See footnote of table 5.III for units.
- Non listed force constant are zeros.

7.4 VROA calculations in (III).

The CID and Raman spectra of (III) will be interpreted as those corresponding to the methyl in equatorial and axial positions at the same time because the mixture is not resolved, and eq. (7.4.1) will be used with a = 0.3 and e = 0.7. Those frequencies assigned to (III) equatorial or axial will have a single valued Δ_z parameter, those ones in which $(III)_e$ and $(III)_a$ superimpose the bands will have a weighted Δ_z. Table 8.III displays the calculated and observed Δ_z. The assignment of frequencies is based in terms of nearest frequencies, PED and the possibility of fitting experimental and calculated sign of Δ_z. In this sense the VROA calculations can help to the assignment of the vibrational spectrum.

The spectrum of (III) presents three big couplets around 960, 500 and 400 cm^{-1}. With the exception of the first, the signs of all of these couplets are correctly predicted as well as the order of magnitude. The first case, couplet associated with Raman bands 969(+) - 946(-) cm^{-1} which belongs to $(III)_e$ and 961(+) cm^{-1} to $(III)_a$, are mainly related to methyl $<C_rCH$ deformations (rockings) though the PED is also scattered in ring stretchings and ring deformations, <CCH. The big couplet corresponding to Raman frequencies of 514(-)-490(+) cm^{-1} can be explained, within these approximations, as two frequencies which belong to $(III)_e$, both of them are principally localized in the in plane internal coordinates of the carbonyl group, ϵ (27 and 33% PED respectively) but contributions arising from ring deformations, <CCH, are also important although their PED are not as concentrated as the in-plane coordinates. The PED of the calculated frequency 486 cm^{-1} for $(III)_a$ is highly concentrated, ϵ(51), and probably will form part of the band centered at 490 cm^{-1} but together will give

rise to a negative theoretical contribution to Δ_z. The couplet associated with 398(+) - 388(-) cm^{-1} has no specific internal coordinate related with it; ring deformations, $\omega_{\alpha\beta}$, have the highest values of PED but also influences of (γ_α, ϵ , χ , ζ , ϕ) would be somehow relevant. No good agreement with experimental observations seems to appear in the region of the torsions.

The zone 1500 - 1400 cm^{-1} mainly possesess all the <HC_rH and <HC_mH deformations. The frequency 1459(+) cm^{-1} can be assigned to an out of phase methyl deformation, with the correct sign predicted. The corresponding in phase frequency can be assigned with confidence to 1421(-) cm^{-1} though in this case VROA calculations do not agree.

The zone 1400 - 700 cm^{-1} contains heavily mixed C-C stretchings and <CCH deformations and no special insight can be inferred. Perhaps the most outstanding features are the negative singlets associated with Raman frequencies 1335(-) cm^{-1} and 1092(-) cm^{-1}. The first can be related to deformations γ_β(46), ζ(19), r_β(9) in PED, with respect to the calculated frequency 1342 cm^{-1} of $(III)_e$, in the frequency 1331 cm^{-1} of $(III)_a$ the main contributions come from γ_α(26), γ_β(40), γ_γ(32), r_β(9). Then, this big negative singlet can arise from <HCH deformations. The other negative singlet at 1092(-) cm^{-1} is related to the calculated frequencies 1087 $(III)_e$ and 1092 cm^{-1} $(III)_a$, the most significant character is a contribution of the stretching C_r-C, R(36), to the frequency of $(III)_e$. The sign in both cases is predicted.

The Raman band at 641 cm^{-1} does not have a well defined sign and corresponds to an out of plane bend of the carbonyl group, ρ(36), and the calculations predict a positive one.

Table 8.III.- VROA calculations of (3R)-(+)-methylcyclohexanone.

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
		1717	1716		
1714	1713	1711	1707	3.09	
			1677		
			1666		
			1638		
			1610		
	1566			7.20	
	1509			2.68	
1467	1465			-3.91	
1455		1456	1459	6.28	2.1
1453	1452		1451	0.12	(+)*
1448		1447		5.96	
1431	1431			-2.31	
1428	1428	1427	1428	3.29	-3.1
1415		1420	1421	3.79	
1385		1377	1381	-3.36	
1365	1361	1360	1361	0.82	(+)*
1342		1345		-4.94	
	1331	1334	1335	-1.85	-7.3
1331	1310(a)	1317	1317	-4.03	-2.8
		1303	1304		(+)*
1295	1298			-1.72	
		1275	1279		(+)*
1269			1268	3.33	-3.0
	1261	1251	1252	-3.60	-5.0
1244	1240			1.71	
1231				-0.93	
1227	1226	1225	1225	0.12	(+)*
	1205	1206	1206	-1.42	(+)*
1197				-0.45	

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
			1187		
1080				-15.85	
			1177		
	1157			1.50	
	1148				
1133				5.48	
1131				-7.83	
	1122	1119	1123	-4.72	(-)
		1115			
1108		1108		-7.63	
1087	1092		1092	-2.87	-15.0
	1072	1080	1081	-1.80	-9.5
		1056	1056		-4.0
1040		1045	1044	4.80	(+)
		1023	1023		-3.4
	998			4.03	
	983			3.45	
971		970	969	-5.27	5.6
	966	960	961	2.51	(+)
955		946	946	-1.15	-5.8
		913			
903	903	886	886	0.32	(+)
			873		(+)
866	868	866	867	4.73	
849	851			-1.76	
828			824	-3.43	3.8
	819	818		-0.61	
803			804	-1.96	
	778	782	782	1.42	
		751	752		(+)
		745	745		
727	730			3.57	
	674	672	672	-1.66	(-)
646		641	641	3.18	(+)

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
	588			5.98	
		546	547		
519		514	514	-3.48	-11.1
489	486	490	490	0.75	9.3
	471	462		-2.84	
		439	439		1.4
	434	427	427	-1.18	-5.3
403			398	5.21	6.3
390	383	386	388	-3.07	-4.7
		369			
	357	363	362		(+)
		345	344		
295		299	298	4.18	-6.6
255	256	259	258	4.12	-20.0
151				-12.07	
142			142		(+)
	136			1.83	
124	125			-6.28	
	116			-4.51	

(a) Double frequency.

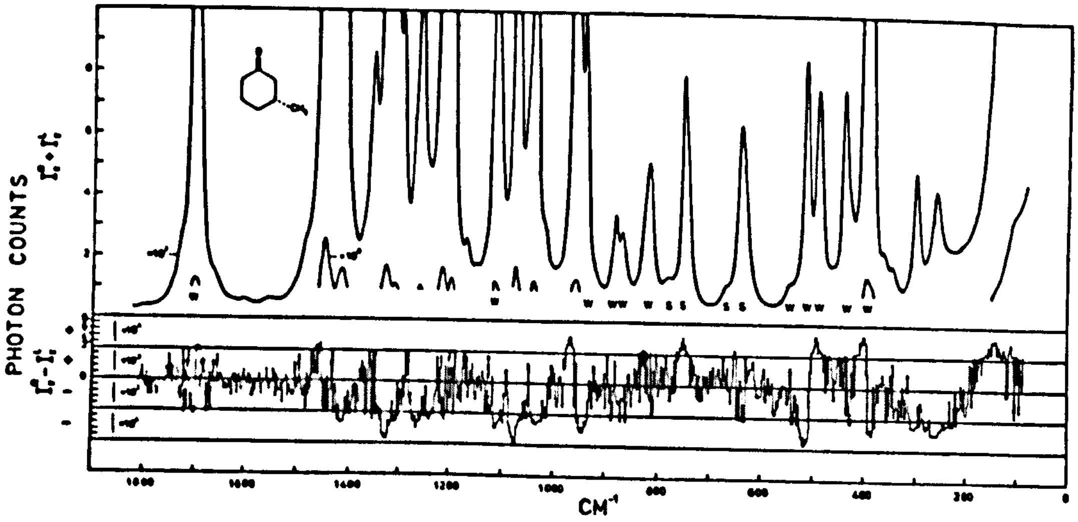
The signs in brackets are not definitive.

Table 8.IV.- VROA calculations for (3R)-(+)-2,2,6,6-tetradeutero-3-methylcyclohexanone.

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta_z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
1707	1707			0.49	
1566				6.75	
1509				2.59	
1465	1467			-1.81	
	1455	1455	1456	7.72	(-)
1452	1453			0.04	
	1448	1445	~1447	5.22	(+)
	1414			4.87	
	1382	1377	1375	-1.17	?
1357	1351		1355	-0.41	(-)
			1336		?
	1324	1324	1324	-1.79	(-)
1305		1307	1310	-3.03	?
1299	1293			-0.83	
1279		1277		-0.18	
1271		1268	1269	-0.32	(-)
1234				-4.97	
	1225			-1.95	
		1212	1211		(+)
1200	1205	1195		1.08	
1177		1178		-0.24	
	1163	1159	1161	-3.80	(+)
1153				-5.55	
	1138			-3.05	
1123	1123	1123	1123	-3.46	(+)
		1117			
1088		1089	1089	3.11	(-)
	1075			7.92	
1050		1066		-8.86	(-)
1043	1044			6.13	

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
	1041			1.32	
1035	1030	1032	1034	-4.03	(+)
1019		1011	1013	-4.30	(-)
	1003	1000		-1.73	
987		964	965	2.60	(+)
954	955	953	950	0.33	(-)
932	929	921	921	0.02	(-)
904	907			3.45	
			890		(-)
	863			-1.77	
844		832	833	1.16	?
815	823			-2.57	
794	790	790	790	0.15	(+)
775				-1.83	
	765		765	-0.41	(-)
	752		750	1.39	(+)
733		727	727	0.73	(+)
714	710			-0.65	
682	678	679	679	-0.58	(-)?
640			640	-0.10	?
	616	612	612	2.01	(+)
562				5.50	
		530	526		?
	486			-1.16	
	463	467	467	8.52	(-)
453		455		-2.76	
425			432	-2.90	(-)
406				-7.08	
		399	396		(+)
	388			-4.51	
	380	377	375	2.72	(+)
	372			-0.76	
366		353	352	2.69	(-)
327			331	1.10	(+)

cal. freq./cm^{-1}		obs. freq./cm^{-1}		$\Delta z/10^{-4}$	
equ.	axi.	IR	Ram.	cal.	obs.
	285	293	293	3.77	(-)
	249	252		1.83	
242			242	1.75	(-)
	143			-12.70	
125	122			-2.90	
113				-3.22	



<u>Figure 8.2</u>.- Raman and VROA spectra of (III).

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CONCLUSIONS

The work carried out in this thesis is an extension of the original formulation of ROA in general, and VROA in particular, within a semiclassical treatment of the interaction radiation-matter. The main achievements we have got are the Stokes-antiStokes asymmetry in resonance scattering Raman, the Fermi resonance processes in VROA, and the polarized-depolarized ratio of intensities. These are aspects theoretically predicted and suitable to be tested experimentally once the new era of multichannel ROA instruments is completely developed. It is interesting to observe that we have not the necessity of intermediate experimental data for realizing the above proposed experiments; therefore, the bond polarizablility and the generalized two-group model approximations are adequated to obtain more insight in the forcasting of these experiments, the succes of which will prove the degree of reliability of the approximations.

The calulations of the depolarized CID show that a better understanding of the force field and electrooptic parameters are necessary in order to achieve a better interpretation of the CID-spectra, and perhaps this new spectroscopy will provide a further test of bond polarizability parameters and force constant refinements.