

Irreducible Representation and Projection Operator Application to Understanding Nonlinear Optical Phenomena: Hyper-Raman, Sum Frequency Generation, and Four-Wave Mixing Spectroscopy

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Symmetry plays an essential role in understanding optical activities of a molecule in infrared and Raman vibrational spectroscopy as well as in nonlinear optical vibrational spectroscopy. Each vibrational mode belongs to an irreducible representation of the underlying symmetry group. In this paper, using the α -helical polypeptide symmetry as an example, we calculate all the third rank nonzero hyper-Raman tensors as well as the infrared and Raman tensors by applying the projection operators to each irreducible species. We demonstrate that the projection operator method provides selection rules for the infrared, Raman, and hyper-Raman vibrational transitions and also other nonlinear optical spectroscopy such as sum frequency generation and the four-, five-, and six-wave mixing coherent vibrational transitions. Specific expressions for all nonzero elements of the corresponding nonlinear susceptibility tensors in a laboratory-fixed coordinate frame are also deduced.

I. Introduction

The development of high-powered and ultrafast lasers as well as advancements in optical technology have enabled nonlinear optical spectroscopy to become one of the most widely attractive and fast growing research areas at present.^{1–8} Nonlinear optical phenomena, such as sum frequency generation (SFG), four-wave mixing like coherent anti-Stokes Raman scattering (CARS), five-wave or six-wave mixing, hyper-Raman (HR) scattering,⁹ etc., arise from a nonlinear response of a sample medium to incident light beams, where the strength of the induced electric field in the medium is proportional to nonlinear susceptibility tensors in a laboratory-fixed (LF) coordinate frame. Such LF susceptibility tensors correspond to molecular hyperpolarizability tensors in a molecule-fixed (MF) coordinate frame. Molecular structural information on the sample medium can be deduced from measurements of such LF tensors. In this paper, we discuss selection rules and relations between the MF tensors and measured LF tensors for several nonlinear optical phenomena, using α -helical polypeptide symmetry as an example.

There are many nonlinear optical processes with (third rank (TR), fourth rank (FR), or higher rank) hyperpolarizability tensors for vibrational transitions. For example, SFG usually involves vibrational transitions related to the TR hyperpolarizability tensor. Since the first surface SFG vibrational spectrum was collected from a monolayer of coumarin dye adsorbed on fused silica in 1987,¹⁰ SFG vibrational spectroscopy (referred to as SFG below) has been developed into a powerful technique to probe important features of surfaces and interfaces at the molecular level. With two incident beams, including a visible laser and a frequency-tunable infrared laser, under the electric dipole approximation, SFG detects enhancement in the second-order nonlinear susceptibility $\chi^{(2)}$ in a

LF coordinate frame, which is related to the TR hyperpolarizability tensor in an MF frame. The SFG intensity is strictly governed by underlying molecular symmetries. Using different polarization combinations of input and output laser beams, various LF tensor components can be probed. By using the transformation property between the two coordinate frames and the symmetries of the resonant molecular vibrations, observed SFG intensities with various polarization combinations can be correlated to the orientation of specific molecules or functional groups on the surface/interface. In the past 2 decades, such general correlations have been deduced explicitly, and extensive research has been performed to investigate orientation information on functional groups and molecules on surfaces and at interfaces.^{11–46}

In this paper, we present a systematic way to deduce selection rules of known molecular symmetry based on projection operators to all irreducible representations of the underlying molecular symmetry group, and relate MF hyperpolarizability tensors to LF susceptibility tensors. We believe that this method is general and also simple enough to be easily adoptable for higher order nonlinear optical processes. Since the transition hyperpolarizability tensor for a typical SFG process can be treated as a product of the (infrared) transition dipole moment and the (Raman) transition polarizability tensor,^{11,15} the method utilizes the infrared and Raman tensors, which are defined by the projections of the dipole moment and polarizability tensors to each irreducible symmetry species, respectively. We show that this systematic method naturally provides not only selections rules for SFG spectroscopy but also the desired expressions for all nonzero elements of $\chi^{(2)}$.

To elucidate the generality of the projection operator method to study higher order nonlinear optical spectroscopy, we also compute TRHR tensors for α -helical symmetry, which automatically give the expected selection rules of the TRHR scattering for the α -helix. In combination with either the infrared or the ordinary Raman tensor, the computed TRHR tensors can

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serve as a basis for studying higher order nonlinear spectroscopy (as the infrared and Raman serve as a basis for SFG study). Even though the general transformation between MF and LF tensors for a higher order nonlinear optical process is already known, it is nontrivial and prone to errors when deriving the desired relations for deducing orientation information in this case. By using the method we introduce here, however, expressions for all the independent nonzero elements of $\chi^{(3)}$ of a four-wave mixing vibrational spectroscopy for α -helical symmetry (either the combined Stokes and anti-Stokes Raman process or the combined infrared and TRHR process) can even be derived by manual computation. Detailed computation results for all nonzero tensor components for α -helical symmetry will be reported elsewhere in the future.⁴⁷ Furthermore, for experiments of higher order nonlinear processes that involve only limited polarization measurements, relations of only part of the tensor components are needed to interpret experimental data. Application of the systematic method discussed in this paper will simplify the data analysis.

One of our research goals is to understand structural information on proteins and peptides of various secondary structural motifs such as the α -helix, using nonlinear spectroscopy. In this paper, we study selection rules and/or relations between LF and MF tensors of the α -helix for SFG, HR scattering, and four-wave mixing, as well as higher order nonlinear optical spectroscopy. We first study the selection rules and symmetries of (relatively) lower order vibrational transitions, such as infrared, Raman, and TRHR processes. With a group theoretical approach of irreducible representations,⁴⁸ Cyvin et al. in 1965⁴⁹ deduced selection rules of the TRHR effects for several molecular symmetry groups, which was followed by further investigations in this direction.^{50–53} On the basis of the projection operator method,^{54,55} we present the TRHR tensors for the α -helix, C_{2v} , and C_{3v} groups that can provide information on both selection rules and relative optical intensities of the corresponding vibrational transitions.

The rest of this paper is arranged as follows: In section 2, we introduce projection operators and investigate their connections to nonlinear optical spectroscopy. In section 3, the proposed projection operator method is applied to α -helical symmetry. The TRHR tensors are explicitly computed, as well as the infrared and Raman tensors. These will serve as a basis for subsequent studies of SFG and higher order nonlinear spectroscopy that can be treated as combinations of infrared, Raman, or HR processes. In section 4, we apply such infrared, Raman, and HR tensors obtained in section 3 to vibrational SFG spectroscopy, and we deduce the relations between LF and MF tensors for orientation analysis of α -helical molecules. In section 5, we demonstrate the feasibility of applying this method to data analysis for higher order nonlinear optical spectroscopy involving four-, five-, and six-wave mixing coherent vibrational transitions. Finally, the methodology is applied to C_{2v} and C_{3v} groups, whose results are summarized for comparison in the Appendix.

II. Irreducible Representations and Optical Phenomena

To deduce vibrational selection rules in the MF frame and relations between the MF and LF frames, we define the basis of an LF coordinate frame by $\hat{1} \equiv \hat{\mathbf{x}} \equiv (1\ 0\ 0)^T$, $\hat{2} \equiv \hat{\mathbf{y}} \equiv (0\ 1\ 0)^T$, and $\hat{3} \equiv \hat{\mathbf{z}} \equiv (0\ 0\ 1)^T$, with hat “ \wedge ” and superscript “ T ” representing a unit vector and the transpose of a matrix, respectively. Let $\{\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\mathbf{c}}\}$ be a normalized basis set for an MF coordinate frame. The transformation \mathbf{R} of a vector from the LF to the MF frame is defined as

$$\mathbf{v}_{MF} = \mathbf{R}\mathbf{v}_{LF} \quad (1)$$

According to the theory of nonlinear optical phenomena, the induced polarization in a medium due to electric fields \mathbf{E}_{ext} of incident light beams can be expanded by

$$P_{ind}^i = \chi_{ij}^{(1)} E_{ext}^j + \chi_{ijk}^{(2)} E_{ext}^j E_{ext}^k + \chi_{ijkl}^{(3)} E_{ext}^j E_{ext}^k E_{ext}^l + \dots \quad (2)$$

where $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are the linear, the second order nonlinear, and the third-order nonlinear susceptibility tensors, respectively. For simplicity in the theory, we have here ignored detailed factors such as Fresnel coefficients and local field corrections in the medium. By convention, any doubly appearing tensor indices indicate summation over all their independent components if there is no specific comment.

To utilize any underlying molecular symmetries, we define the induced molecular dipole moment μ_{ind} in the MF frame by

$$\mu_{ind}^i = \alpha_{ij} E_{MF}^j + \beta_{ijk} E_{MF}^j E_{MF}^k + \gamma_{ijkl} E_{MF}^j E_{MF}^k E_{MF}^l + \dots \quad (3)$$

where α is molecular polarizability, β and γ are the TR and the FR hyperpolarizability, respectively, and $\mathbf{E}_{MF} \equiv \mathbf{R}\mathbf{E}_{ext}$. With N being the average molecular number density in the medium, the induced polarization in the LF frame is found to be

$$\mathbf{P}_{ind} = N\mathbf{R}^{-1}\mu_{ind} \quad (4)$$

where superscript “ -1 ” represents the matrix inverse. This implicitly defines the general relations between MF and LF tensors as

$$\begin{aligned} \chi_{ij}^{(1)} &\equiv N R_{im}^{-1} \alpha_{mj} R_{nj}, \quad \chi_{ijk}^{(2)} \equiv N R_{im}^{-1} \beta_{mns} R_{nj} R_{sk}, \\ \chi_{ijkl}^{(3)} &\equiv N R_{im}^{-1} \gamma_{mnst} R_{nj} R_{sk} R_{tl}, \dots \end{aligned} \quad (5)$$

Then, under the harmonic oscillator approximation, the optical intensities due to P_{ind}^i for the typical Raman and HR transitions from the ground states [Figure 1, parts a–d] are proportional to, respectively,^{1,2,48,56}

$$I_{Raman}^{i:vg} \propto N |R_{im}^{-1} \langle v | \tilde{\alpha}_{mj} | g \rangle E_{MF}^n|^2 \quad (6)$$

$$I_{TRHR}^{i:vg} \propto N |R_{im}^{-1} \langle v | \tilde{\beta}_{mns} | g \rangle E_{MF}^n E_{MF}^s|^2 \quad (7)$$

$$I_{FRHR}^{i:vg} \propto N |R_{im}^{-1} \langle v | \tilde{\gamma}_{mnst} | g \rangle E_{MF}^n E_{MF}^s E_{MF}^t|^2 \quad (8)$$

where $|g\rangle$ and $|v\rangle$ represent the ground state and arbitrary excited vibrational states in the MF coordinate frame, respectively, and the symbol “ \sim ” represents a quantum mechanical operator acting on either a bra or ket vector. On the other hand, the intensity for the infrared transition from the ground state [Figure 1e] with a beam polarization direction of \hat{i} in the LF frame is proportional to

$$I_{infrared}^{i:vg} \propto N |R_{im}^{-1} \langle v | \tilde{\mu}_m | g \rangle|^2 \quad (9)$$

where $\tilde{\mu}$ is the operator for molecular electric dipole moment μ in the MF frame. It should be mentioned that optical intensities are proportional to N^2 for coherent processes such as SFG, CARS, etc.

Following the theory of molecular vibrations,⁴⁸ vibrational states of a molecule are classified into the irreducible representations of the underlying symmetry group \mathbf{G} that preserves the total Hamiltonian of the system. Orthogonality between vibrations belonging to different symmetry species corresponds

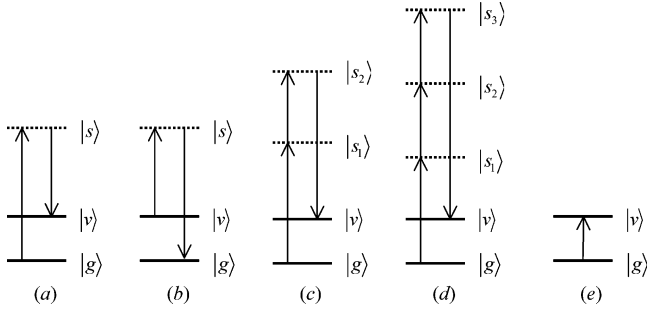


Figure 1. Schematic vibrational transitions for typical Raman, HR, and infrared effects: (a) Stokes Raman, (b) anti-Stokes Raman, (c) TRHR, (d) fourth rank HR (FRHR), and (e) infrared. $|g\rangle$ and $|v\rangle$ represent the ground state and an excited vibrational state, respectively, while $|s\rangle$ and $|s_i\rangle$ represent arbitrary (virtual or real) excited states.

to the orthogonality of the irreducible representations $\Gamma^{(i)}$ of \mathbf{G} :

$$\sum_{g \in \mathbf{G}} [\Gamma^{(i)}(g)]_{lm}^{-1} [\Gamma^{(j)}(g)]_{st} = \frac{|\mathbf{G}|}{f_i} \delta_{ij} \delta_{ms} \delta_{lt} \quad (10)$$

where $|\mathbf{G}|$ is the number of all group elements and f_i is the dimension of the i th irreducible representation $\Gamma^{(i)}$. This naturally defines the projection operator \mathbf{P}_Γ to a particular symmetry species Γ of \mathbf{G} by^{54,55}

$$\mathbf{P}_\Gamma \equiv \frac{f_\Gamma}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \{\chi_\Gamma(g)\}^* \mathbf{O}_g \quad (11)$$

$$\sum_\Gamma \mathbf{P}_\Gamma = \mathbf{1} \quad (12)$$

where $\chi_\Gamma(g)$ are the characters of the irreducible representation Γ , superscript “*” represents the complex conjugate, and \mathbf{O}_g s are suitable transformation operators corresponding to each element g of \mathbf{G} and acting on quantities defined in the MF frame. The usefulness of \mathbf{P}_Γ in infrared and Raman spectroscopy has already been well established. As an example, the infrared activity of vibrations belonging to the irreducible representation Γ is specifically determined by

$$\mu_{vg}^\Gamma \equiv \langle v | \tilde{\mu}^\Gamma | g \rangle \equiv \langle v | \mathbf{P}_\Gamma \tilde{\mu} | g \rangle \equiv \mathbf{P}_\Gamma \mu^{vg} \quad (13)$$

with $\mu^\Gamma \equiv \mathbf{P}_\Gamma \mu$ (infrared tensor) and $\mu^{vg} \equiv \langle v | \tilde{\mu} | g \rangle$. This is because (9) can be expressed as

$$\begin{aligned} I_{infrared}^{i,vg} &\propto N |R_{im}^{-1} \langle v | (\sum_\Gamma \mathbf{P}_\Gamma \tilde{\mu})_m | g \rangle|^2 \\ &\quad \text{[insert the identity of (12)]} \\ &= \sum_{\Gamma, \Gamma'} N \langle g | (R_{im}^{-1} \tilde{\mu}_m^\Gamma)^* | v \rangle \langle v | R_{im}^{-1} \tilde{\mu}_m^{\Gamma'} | g \rangle \\ &= \sum_\Gamma N |R_{im}^{-1} \langle v | \tilde{\mu}_m^\Gamma | g \rangle|^2 \text{ [from (10)]} \\ &= \sum_\Gamma N |i^T \mathbf{R}^{-1} \mu_{vg}^\Gamma|^2 \end{aligned} \quad (14)$$

where the summations over Γ and Γ' are reduced to a summation over Γ due to the orthogonality between different irreducible representations. Similarly, the optical activities for the Raman and TRHR transitions from the ground state $|g\rangle$ are determined by, respectively

$$\alpha_{vg}^\Gamma \equiv \langle v | \tilde{\alpha}^\Gamma | g \rangle \equiv \langle v | \mathbf{P}_\Gamma \tilde{\alpha} | g \rangle \equiv \mathbf{P}_\Gamma \alpha^{vg} \quad (15)$$

$$\beta_{vg}^\Gamma \equiv \langle v | \tilde{\beta}^\Gamma | g \rangle \equiv \langle v | \mathbf{P}_\Gamma \tilde{\beta} | g \rangle \equiv \mathbf{P}_\Gamma \beta^{vg} \quad (16)$$

with $\alpha^\Gamma \equiv \mathbf{P}_\Gamma \alpha$ (Raman tensor), $\beta^\Gamma \equiv \mathbf{P}_\Gamma \beta$ (TRHR tensor), $\alpha^{vg} \equiv \langle v | \tilde{\alpha} | g \rangle$, and $\beta^{vg} \equiv \langle v | \tilde{\beta} | g \rangle$. For specific computations of these tensors, it is efficient to construct each operator \mathbf{O}_g in (11) by a 3×3 matrix on the basis of $\{\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\mathbf{c}}\}$. Considering the transformations of μ , α , and β under the operation \mathbf{O}_g , projections of these to an irreducible representation Γ are found to be, respectively,

$$\mu^\Gamma = \frac{f_\Gamma}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \{\chi_\Gamma(g)\}^* \mathbf{O}_g \mu \quad (17)$$

$$\alpha^\Gamma = \frac{f_\Gamma}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \{\chi_\Gamma(g)\}^* \mathbf{O}_g \alpha [\mathbf{O}_g]^{-1} \quad (18)$$

$$\beta_i^\Gamma \equiv (\beta^\Gamma)_i = \frac{f_\Gamma}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \{\chi_\Gamma(g)\}^* [\mathbf{O}_g^T]^{-1} \{\mathbf{O}_g \beta\}_i \mathbf{O}_g^{-1} \quad (19)$$

where β_i represents a 3×3 matrix such that $[\beta_i]_{mn} = \beta_{imn}$ and $\{\mathbf{O}_g \beta\}_i \equiv [\mathbf{O}_g]_{im} \beta_m$. For α -helical symmetry, these tensors are explicitly computed and applied to SFG and four-, five- and six-wave mixing vibrational spectroscopies. To facilitate understanding of the subject, similar analyses for molecules of C_{2v} and C_{3v} symmetries are presented in the Appendix.

III. Infrared, Raman, and TRHR Processes for α -Helical Symmetry

The α -helix is one of the major conformations in polypeptides and globular proteins. Its regular structure is defined by a translation $h = 1.495 \text{ \AA}$ and a rotation $\psi = 2\pi/3.615$ per each amino acid residue along the helical axis,^{57,58} which we define as the c -axis so that $\hat{\mathbf{c}} = \hat{\mathbf{a}} \times \hat{\mathbf{b}}$ in a MF frame [Figure 2], corresponding to the number of residues $u \approx 18$ in a crystallographic unit cell along the c -axis. Since translations do not affect any internal vibrations, the vibrational symmetry species can be completely deduced from the u -fold rotation about the helix axis, viz., $\mathbf{G} = \{\mathbf{E}, \mathbf{H}(\psi), \mathbf{H}^2(\psi), \dots, \mathbf{H}^{u-1}(\psi)\}$, which defines a desired set of symmetry operations \mathbf{O}_g to be used for (11) with

$$\mathbf{H}(\psi) = \begin{pmatrix} \cos \psi & -\sin \psi & 0 \\ \sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (20)$$

If θ is the phase difference between adjacent chemical repeat units, the values of θ for optically active vibrations are discrete due to the u -fold rotation axis of symmetry:

$$\theta_t = t\psi \quad (t = 0, \pm 1, \dots, \pm[u-1]) \quad (21)$$

This classifies symmetries of all possible vibrations into irreducible representations of one dimension, labeled as $\Gamma(\theta_t)$, whose characters are given by⁵⁹

$$\chi_{\theta_t}(\mathbf{H}^s) = e^{is\theta_t} \quad (s = 0, 1, \dots, u-1) \quad (22)$$

Except for the cases of real χ_θ (e.g., $\Gamma(\theta) = A$ for $\theta = 0$ and $\Gamma(\theta) = B$ for $\theta = t\psi = \pm\pi$), the normal-mode frequencies are degenerate in pairs belonging to $\Gamma(t\psi) = E_t$ and $\Gamma(-t\psi) = E_{-t}$, respectively.

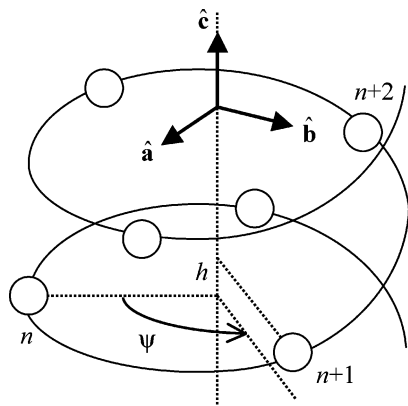


Figure 2. Definition of an MF frame for a regular helical molecule.

To facilitate computations of the infrared and Raman tensors for the α -helical symmetry, we consider the following unitary transformation:

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i & 0 \\ 1 & -i & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix} \quad (23)$$

where $\mathbf{U}^{-1} = \mathbf{U}^\dagger$ with superscript “ \dagger ” representing the Hermetian conjugate of a matrix. This diagonalizes \mathbf{H}^s by

$$\mathbf{U}\mathbf{H}^s\mathbf{U}^{-1} = \begin{pmatrix} e^{is\psi} & 0 & 0 \\ 0 & e^{-is\psi} & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \Lambda^s \quad (24)$$

From (17) and (18) with $|\mathbf{G}| = u$, we have

$$\boldsymbol{\mu}^{\theta_t} = \mathbf{U}^{-1} \left(\sum_{u_s=0}^{u-1} e^{-ist\psi} \Lambda^s \right) \mathbf{U} \boldsymbol{\mu} \quad (25)$$

$$\boldsymbol{\alpha}^{\theta_t} = \mathbf{U}^{-1} \left(\sum_{u_s=0}^{u-1} e^{-ist\psi} \Lambda^s [\mathbf{U} \boldsymbol{\alpha} \mathbf{U}^{-1}] \Lambda^{-s} \right) \mathbf{U} \quad (26)$$

Thus, we have the following list of infrared and Raman tensors for molecules of regular α -helical symmetry:^{60,61}

$$\boldsymbol{\mu}^A = (0 \ 0 \ \mu_c)^T \quad (27)$$

$$\boldsymbol{\mu}^{E_1} = \frac{1}{2} (\mu_a + i\mu_b \quad -i[\mu_a + i\mu_b] \quad 0)^T \quad (28)$$

$$\boldsymbol{\mu}^{E_2} = \mathbf{0} \quad (29)$$

$$\boldsymbol{\alpha}^A = \frac{1}{2} \begin{pmatrix} \alpha_{aa} + \alpha_{bb} & \alpha_{ab} - \alpha_{ba} & 0 \\ \alpha_{ba} - \alpha_{ab} & \alpha_{aa} + \alpha_{bb} & 0 \\ 0 & 0 & 2\alpha_{cc} \end{pmatrix} \quad (30)$$

$$\boldsymbol{\alpha}^{E_1} = \frac{1}{2} \begin{pmatrix} 0 & 0 & \alpha_{ac} + i\alpha_{bc} \\ 0 & 0 & -i(\alpha_{ac} + i\alpha_{bc}) \\ \alpha_{ca} + i\alpha_{cb} & -i(\alpha_{ca} + i\alpha_{cb}) & 0 \end{pmatrix} \quad (31)$$

$$\boldsymbol{\alpha}^{E_2} = \frac{1}{4} \times \begin{pmatrix} \alpha_{aa} - \alpha_{bb} + i(\alpha_{ab} + \alpha_{ba}) & \alpha_{ab} + \alpha_{ba} - i(\alpha_{aa} - \alpha_{bb}) & 0 \\ \alpha_{ab} + \alpha_{ba} - i(\alpha_{aa} - \alpha_{bb}) & -\alpha_{aa} + \alpha_{bb} - i(\alpha_{ab} + \alpha_{ba}) & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (32)$$

$$\boldsymbol{\alpha}^{E_3} = \mathbf{0} \quad (33)$$

Infrared and Raman tensors are zeros for all $E_{\pm t}$ -species vibrations of the α -helical symmetry with $t > 2$. As shown in (27)–(29), the infrared vibrational transitions are active only for the A- or E_1 -species, where vibrations of the A-species are parallel and those of the E_1 -species are perpendicular to the helix axis. In the Raman vibrational shifts, E_2 -modes (perpendicular to the helix axis) are also active as well as the A- and E_1 -modes.

Detailed information about TRHR spectroscopy can be found in a review article by Ziegler⁹ or references therein. Although selection rules for the vibrational TRHR shifts for helical polymer molecules were investigated by Fanconi and Peticolas long ago,⁵⁰ there has been no information about the specific tensor form of each irreducible species. In this paper, we report all the nonzero TRHR tensors for the α -helical symmetry, which are important in understanding such nonlinear optical phenomena as four-, five-, and six-wave mixing vibrational transitions.

In a similar way as that used for the infrared and Raman tensors, projections of $\boldsymbol{\beta}$ to the θ_t -species can be obtained from

$$\boldsymbol{\beta}_i^{\theta_t} = \mathbf{U}^{-1} \left\{ \sum_{u_s=0}^{u-1} e^{-ist\psi} \Lambda^s \mathbf{U} [\mathbf{H}^s \boldsymbol{\beta}]_i \mathbf{U}^{-1} \Lambda^{-s} \right\} \mathbf{U} \quad (34)$$

where with $\mathbf{N} \equiv (\boldsymbol{\beta}_a + i\boldsymbol{\beta}_b)/2$, $\mathbf{H}^s \boldsymbol{\beta}$ can be represented by

$$\mathbf{H}^s \boldsymbol{\beta} = (\mathbf{N} e^{is\psi} + \mathbf{N}^* e^{-is\psi} \quad -i\mathbf{N} e^{is\psi} + i\mathbf{N}^* e^{-is\psi} \quad \boldsymbol{\beta}_c)^T \quad (35)$$

Since $[\mathbf{H}^s \boldsymbol{\beta}]_c = \boldsymbol{\beta}_c$, it is evident that $\boldsymbol{\beta}_c^{\theta_t}$ has the same form as $\boldsymbol{\alpha}^{\theta_t}$. We list only $\boldsymbol{\beta}_a^{\theta_t}$ and $\boldsymbol{\beta}_b^{\theta_t}$ for the TRHR tensors below.

$$\boldsymbol{\beta}_a^A = \frac{1}{2} \begin{pmatrix} 0 & 0 & \beta_{aac} + \beta_{bbc} \\ 0 & 0 & \beta_{abc} - \beta_{bca} \\ \beta_{aca} + \beta_{bcb} & \beta_{acb} - \beta_{bca} & 0 \end{pmatrix} \quad (36)$$

$$\boldsymbol{\beta}_b^A = \frac{1}{2} \begin{pmatrix} 0 & 0 & \beta_{bac} - \beta_{abc} \\ 0 & 0 & \beta_{aac} + \beta_{bbc} \\ \beta_{bca} - \beta_{acb} & \beta_{aca} + \beta_{bcb} & 0 \end{pmatrix} \quad (37)$$

$$\boldsymbol{\beta}_a^{E_1} = \frac{1}{2} \begin{pmatrix} \eta_{aaa}^{E_1} & \eta_{aab}^{E_1} & 0 \\ \eta_{aba}^{E_1} & \eta_{aaa}^{E_1} & 0 \\ 0 & 0 & \beta_{acc} + i\beta_{bcc} \end{pmatrix} \quad (38)$$

$$\boldsymbol{\beta}_b^{E_1} = \frac{1}{2} \begin{pmatrix} -i\eta_{aaa}^{E_1} & \eta_{bab}^{E_1} & 0 \\ \eta_{bba}^{E_1} & -i\eta_{aaa}^{E_1} & 0 \\ 0 & 0 & \beta_{bcc} - i\beta_{acc} \end{pmatrix} \quad (39)$$

$$\boldsymbol{\beta}_a^{E_2} = \frac{1}{2} \begin{pmatrix} 0 & 0 & \eta_{aac}^{E_2} \\ 0 & 0 & -i\eta_{aac}^{E_2} \\ \eta_{aca}^{E_2} & -i\eta_{aca}^{E_2} & 0 \end{pmatrix} \quad (40)$$

$$\boldsymbol{\beta}_b^{E_2} = -i\boldsymbol{\beta}_a^{E_2} \quad (41)$$

$$\boldsymbol{\beta}_a^{E_3} = \frac{1}{2} \begin{pmatrix} \eta_{aaa}^{E_3} & \eta_{aab}^{E_3} & 0 \\ \eta_{aab}^{E_3} & -\eta_{aaa}^{E_3} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (42)$$

$$\boldsymbol{\beta}_b^{E_3} = -i\boldsymbol{\beta}_a^{E_3} \quad (43)$$

$$\boldsymbol{\beta}_i^{E_4} = \mathbf{0} \quad (44)$$

with

$$\begin{aligned} \eta_{aaa}^{E_1} &\equiv \frac{1}{2}\{\beta_{aaa} + \beta_{abb} + i[\beta_{baa} + \beta_{bbb}]\} \\ \eta_{aab}^{E_1} &\equiv \frac{1}{4}\{3\beta_{aab} - \beta_{aba} - \beta_{baa} + \beta_{bbb} + \\ &\quad i[\beta_{bab} - 3\beta_{bba} - \beta_{aaa} + \beta_{abb}]\} \\ \eta_{aba}^{E_1} &\equiv \frac{1}{4}\{3\beta_{aba} - \beta_{aab} - \beta_{baa} + \beta_{bbb} + \\ &\quad i[\beta_{bba} - 3\beta_{bab} - \beta_{aaa} + \beta_{abb}]\} \\ \eta_{bab}^{E_1} &\equiv \frac{1}{4}\{3\beta_{bab} - \beta_{bba} + \beta_{aaa} - \beta_{abb} + \\ &\quad i[3\beta_{aba} - \beta_{aab} - \beta_{baa} + \beta_{bbb}]\} \\ \eta_{bba}^{E_1} &\equiv \frac{1}{4}\{3\beta_{bba} - \beta_{bab} + \beta_{aaa} - \beta_{abb} + \\ &\quad i[3\beta_{aab} - \beta_{aba} - \beta_{baa} + \beta_{bbb}]\} \\ \eta_{aac}^{E_2} &\equiv \frac{1}{2}\{\beta_{aac} - \beta_{bcc} + i[\beta_{bac} + \beta_{abc}]\} \\ \eta_{aca}^{E_2} &\equiv \frac{1}{2}\{\beta_{aca} - \beta_{bcb} + i[\beta_{bca} + \beta_{acb}]\} \\ \eta_{aaa}^{E_3} &\equiv \frac{1}{4}\{\beta_{aaa} - \beta_{abb} - \beta_{bab} - \beta_{bba} + \\ &\quad i[\beta_{baa} - \beta_{bbb} + \beta_{aab} + \beta_{aba}]\} \\ \eta_{aab}^{E_3} &\equiv \frac{1}{4}\{\beta_{baa} - \beta_{bbb} + \beta_{aab} + \beta_{aba} + \\ &\quad i[\beta_{bab} + \beta_{bba} - \beta_{aaa} + \beta_{abb}]\} \end{aligned}$$

Thus, E_3 -species vibrations (forbidden in the infrared and Raman transitions) can be optically active in the TRHR transitions, in addition to the A -, E_1 -, and E_2 -modes.

IV. Vibrational SFG Spectroscopy for α -Helical Symmetry

A. Optical Selection Rules. SFG is involved in a broad range of nonlinear photonic energy transitions. In this paper, SFG refers to the nonlinear optical process shown in Figure 3a. According to the quantum mechanical description, the component of the hyperpolarizability tensor related to the vibrationally resonant SFG process of two incident beams of frequencies ω_1 (visible light) and ω_2 (infrared light) can be expressed by¹⁵

$$\beta_{ijk} = \sum_v \langle g | \tilde{\alpha}_{ij}(\omega_{SF}, \omega_1) | v \rangle \langle v | \tilde{\mu}_k(\omega_2) | g \rangle \frac{\rho_g^{(0)} - \rho_v^{(0)}}{\omega_2 - \omega_v + i\Gamma_v} \quad (45)$$

where $\omega_{SF} \equiv \omega_1 + \omega_2$ and ω_v is the frequency of the vibrational transition from $|g\rangle$ to $|v\rangle$ with $\rho_g^{(0)}$ and $\rho_v^{(0)}$ being their fractional populations, respectively, and Γ_v being the corresponding line width parameter. Using the identity relation of (12), the transition tensor terms within the summation are expressed by

$$\begin{aligned} \langle g | \tilde{\alpha}_{ij} | v \rangle \langle v | \tilde{\mu}_k | g \rangle &= \langle g | \sum_{\Gamma} (\mathbf{P}_{\Gamma} \tilde{\alpha})_{ij} | v \rangle \langle v | \sum_{\Gamma} (\mathbf{P}_{\Gamma} \tilde{\mu})_k | g \rangle \\ &= \sum_{\Gamma} \langle g | \tilde{\alpha}_{ij}^{\Gamma} | v \rangle \langle v | \tilde{\mu}_k^{\Gamma} | g \rangle. \quad [\text{from (10)}] \quad (46) \end{aligned}$$

This corresponds to the fact that if vibrations belonging to a symmetry species Γ are excited, the very excited vibrations of

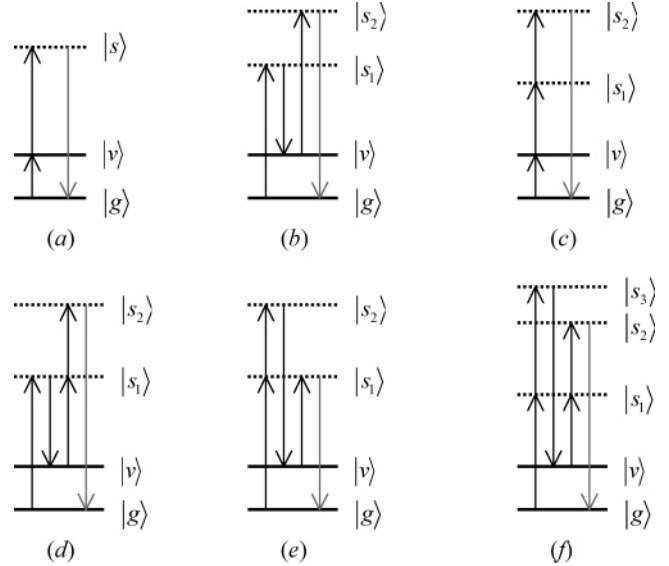


Figure 3. Typical nonlinear vibrational processes: (a) SFG process of $[\alpha^{vg\dagger}_{ij}\mu_k^{vg}]$, (b) $[\alpha^{vg\dagger}_{ij}\alpha_{kl}^{vg}]$, (c) $[\beta_i^{vg\dagger}\mu_j^{vg}\mu_l^{vg}]$, (d) $[\alpha^{vg\dagger}_{ij}\beta_{klm}^{vg}]$, (e) $[\beta_i^{vg\dagger}\mu_j^{vg}\mu_l^{vg}]$, and (f) $[\beta_i^{vg\dagger}\mu_j^{vg}\mu_l^{vg}]$.

the Γ -species transit back to the ground state. Thus, (45) can be rewritten as

$$\beta_{ijk} = \sum_{\Gamma} \sum_v [\beta_{vg}^{\Gamma}]_{ijk} \frac{\rho_g^{(0)} - \rho_v^{(0)}}{\omega_2 - \omega_v + i\Gamma_v} \equiv \sum_{\Gamma} \beta_{ijk}^{\Gamma} \quad (47)$$

with

$$[\beta_{vg}^{\Gamma}]_{ijk} \equiv \langle g | \tilde{\alpha}_{ij}^{\Gamma} | v \rangle \langle v | \tilde{\mu}_k^{\Gamma} | g \rangle = [\alpha_{vg}^{\Gamma}]_{ji}^* [\mu_{vg}^{\Gamma}]_k \quad (48)$$

Values of all desired transition tensor elements can be obtained by expanding each involved tensor in terms of normal coordinates at molecular equilibrium. Derivation of the normal coordinates for helical structures can be found elsewhere.⁶¹ Considering up to linear terms in \mathbf{q}^{Γ} , i.e., dimensionless normal coordinates for the Γ -species, (48) becomes

$$[\beta_{vg}^{\Gamma}]_{ijk} = \sum_r \left(\frac{\partial \alpha_{ji}^{\Gamma}}{\partial q_r^{\Gamma(\theta)}} \right)_{eq}^* \left(\frac{\partial \mu_k^{\Gamma}}{\partial q_r^{\Gamma(\theta)}} \right)_{eq} |\langle v | \tilde{q}_r^{\Gamma(\theta)} | g \rangle|^2 \quad (49)$$

In general vibrational transitions under the harmonic oscillator approximation, the matrix elements for nondegenerate modes are given by

$$\langle v_r | \tilde{q}_r^{\Gamma} | v_r - 1 \rangle = \langle v_r - 1 | \tilde{q}_r^{\Gamma} | v_r \rangle = \sqrt{\frac{v_r}{2}} \quad (50)$$

For 2-fold degenerate vibrations of $\Gamma(\theta)$ and $\Gamma(-\theta)$, which are perpendicular to the helix axis, the r th dimensionless normal coordinate is decomposed into the a - and b -axis components by $q_r^{\Gamma(\theta)} = q_{ra}^{\Gamma} + iq_{rb}^{\Gamma}$ with $q_{ra}^{\Gamma} = \text{Re}\{q_r^{\Gamma(\theta)}\}$ and $q_{rb}^{\Gamma} = \text{Im}\{q_r^{\Gamma(\theta)}\}$, and their matrix elements are found to be^{62,63}

$$\langle v_r + 1, l_r \pm 1 | \tilde{q}_r^{\Gamma(\pm\theta)} | v_r, l_r \rangle = \mp \sqrt{\frac{1}{2}(v_r \pm l_r + 2)} \quad (51)$$

$$\langle v_r - 1, l_r \pm 1 | \tilde{q}_r^{\Gamma(\pm\theta)} | v_r, l_r \rangle = \pm \sqrt{\frac{1}{2}(v_r \mp l_r)} \quad (52)$$

with l_r being vibrational angular momentum quantum numbers where $|l_r|$ may take the integral values $\nu_r, \nu_r - 2, \dots, 1$ or 0.

The SFG intensities for α -helical molecules are affected only by modes belonging to the A- and E₁-species, since $\boldsymbol{\mu}^{E_2} = \mathbf{0}$ [see (29)]. As an example, considering the A-species vibrations and applying (27) and (30) to (48) with $\boldsymbol{\alpha}^T = \boldsymbol{\alpha}$, we have

$$[\beta_{vg}^A]_{ijk} = \frac{1}{2} \begin{pmatrix} \alpha_{aa}^{vg} + \alpha_{bb}^{vg} & 0 & 0 \\ 0 & \alpha_{aa}^{vg} + \alpha_{bb}^{vg} & 0 \\ 0 & 0 & 2\alpha_{cc}^{vg} \end{pmatrix}^* \begin{pmatrix} 0 \\ 0 \\ \mu_c^{vg} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ \mu_c^{vg} \end{pmatrix} \quad (53)$$

Thus, the nonzero elements of β_{ijk}^A are such elements that are diagonal in (i, j) and $k = c$. Using the same method, it is trivial to deduce the MF hyperpolarizability tensor elements for the E₁-species vibrations. Therefore, the SFG selection rules can be obtained based on those of infrared and Raman, which were derived from projection operators to irreducible representations.

The corresponding susceptibility tensor elements in the LF frame are given by

$$\chi_{ijk}^{(2)} = \sum_{\Gamma} \sum_v [\chi_{vg}^{\Gamma}]_{ijk} \frac{\rho_g^{(0)} - \rho_v^{(0)}}{\omega_2 - \omega_v + i\Gamma_v} \equiv \sum_{\Gamma} [\chi_{\Gamma}^{(2)}]_{ijk} \quad (54)$$

with $[\chi_{vg}^{\Gamma}]_{ijk} \equiv NR_{im}^{-1} [\chi_{vg}^{\Gamma}]_{mms} R_{nj} R_{sk}$. The related SFG intensity is proportional to

$$I_{SFG} \propto |\chi_{ijk}^{(2)} E_{ext}^j E_{ext}^k|^2 = \left| \sum_{\Gamma} [\chi_{\Gamma}^{(2)}]_{ijk} E_{ext}^j E_{ext}^k \right|^2 \quad (55)$$

In this case, since $[\chi_{\Gamma(-\theta)}^{(2)}]_{ijk} = [\chi_{\Gamma(\theta)}^{(2)*}]_{ijk}$, the elements of $\chi^{(2)}$ are simply given by

$$\chi_{ijk}^{(2)} = [\chi_A^{(2)}]_{ijk} + 2\text{Re}\{[\chi_{E_1}^{(2)}]_{ijk}\} \quad (56)$$

B. Molecular Orientation on a Surface. Information about molecular orientations relative to a sample surface, to which the z-axis in the LF frame is chosen to be normal, can be derived from observed optical intensities with polarized light beams. For this purpose, we specifically define the transformation matrix \mathbf{R} between the LF and MF frames by

$$\mathbf{R}(\chi, \theta, \phi) = \begin{pmatrix} c_{\chi} c_{\theta} c_{\phi} - s_{\chi} s_{\phi} & s_{\chi} c_{\theta} c_{\phi} + c_{\chi} s_{\phi} & -s_{\theta} c_{\phi} \\ -c_{\chi} c_{\theta} s_{\phi} - s_{\chi} c_{\phi} & -s_{\chi} c_{\theta} s_{\phi} + c_{\chi} c_{\phi} & s_{\theta} s_{\phi} \\ c_{\chi} s_{\theta} & s_{\chi} s_{\theta} & c_{\theta} \end{pmatrix} \quad (57)$$

where $c \equiv \cos$, $s \equiv \sin$, and χ , θ , and ϕ are Euler angles whose definition can be found elsewhere.¹⁶ Upon averaging is performed over χ and ϕ except for the angle θ defined by $c_{\theta} \equiv \hat{\mathbf{c}} \cdot \hat{\mathbf{z}}$, there are seven independent expressions for nonzero elements of $\chi^{(2)}$ in the LF frame:

$$\chi_{zzz}^{(2)} = \frac{N}{2} \{2\beta_{ccc} c_{\theta}^2 + (\beta_{aac} + \beta_{aca} + \beta_{caa} + \beta_{bbc} + \beta_{bcc} + \beta_{cbb}) s_{\theta}^2\} c_{\theta} \quad (58)$$

$$\chi_{xxz}^{(2)} = \frac{N}{4} \{(\beta_{aac} + \beta_{bbc})(c_{\theta}^2 + 1) + (2\beta_{ccc} - \beta_{aca} - \beta_{caa} - \beta_{bcc} - \beta_{cbb}) s_{\theta}^2\} c_{\theta} = \chi_{yyz}^{(2)} \quad (59)$$

$$\chi_{xzx}^{(2)} = \frac{N}{4} \{(\beta_{aca} + \beta_{bcc})(c_{\theta}^2 + 1) + (2\beta_{ccc} - \beta_{aac} - \beta_{caa} - \beta_{bbc} - \beta_{cbb}) s_{\theta}^2\} c_{\theta} = \chi_{zyz}^{(2)} \quad (60)$$

$$\chi_{zxx}^{(2)} = \frac{N}{4} \{(\beta_{caa} + \beta_{cbb})(c_{\theta}^2 + 1) + (2\beta_{ccc} - \beta_{aac} - \beta_{aca} - \beta_{bbc} - \beta_{bcc}) s_{\theta}^2\} c_{\theta} = \chi_{zyy}^{(2)} \quad (61)$$

$$\chi_{xyz}^{(2)} = \frac{N}{4} \{2(\beta_{abc} - \beta_{bac}) c_{\theta}^2 - (\beta_{acb} - \beta_{cab} - \beta_{bca} + \beta_{cba}) s_{\theta}^2\} = -\chi_{yxz}^{(2)} \quad (62)$$

$$\chi_{xzy}^{(2)} = \frac{N}{4} \{2(\beta_{acb} - \beta_{bca}) c_{\theta}^2 - (\beta_{abc} + \beta_{cab} - \beta_{bac} - \beta_{cba}) s_{\theta}^2\} = -\chi_{zyx}^{(2)} \quad (63)$$

$$\chi_{zxy}^{(2)} = \frac{N}{4} \{2(\beta_{cab} - \beta_{cba}) c_{\theta}^2 + (\beta_{abc} - \beta_{acb} - \beta_{bac} + \beta_{bca}) s_{\theta}^2\} = -\chi_{zyx}^{(2)} \quad (64)$$

These relations hold for the TRHR process [Figure 1c] or for the vibrational SFG effects without any underlying molecular symmetry. More general relations without averaging over χ and ϕ can be found in the article by Hirose et al.¹⁶

In the presence of molecular symmetries, some elements of $\boldsymbol{\beta}^{\Gamma}$ for the SFG process become zero.³⁹ Fortunately, using (48) with the calculated infrared tensor $\boldsymbol{\mu}^{\Gamma}$ and Raman tensor $\boldsymbol{\alpha}^{\Gamma}$, we can easily deduce all nonzero elements of $\boldsymbol{\beta}^{\Gamma}$ for each irreducible species. Moreover, since $\mathbf{R}^{-1} = \mathbf{R}^T$ with \mathbf{R} given by (57), the values of $[\chi_{vg}^{\Gamma}]_{ijk}$ are obtained by

$$[\chi_{vg}^{\Gamma}]_{ijk} = N \{(\mathbf{R}\hat{i})^T [\boldsymbol{\alpha}_{vg}^{\Gamma}]^{\dagger} (\mathbf{R}\hat{j})\} \{[\boldsymbol{\mu}_{vg}^{\Gamma}]^T (\mathbf{R}\hat{k})\} \quad (65)$$

where $\mathbf{R}\hat{i}$ is found to be the i th column vector of \mathbf{R} . In view of (53), for the A-species of (58), we have

$$\begin{aligned} [\chi_{vg}^A]_{zzz} &= \frac{N}{2} \{2[\beta_{vg}^A]_{ccc} c_{\theta}^2 + ([\beta_{vg}^A]_{aac} + [\beta_{vg}^A]_{bbc}) s_{\theta}^2\} c_{\theta} \\ &= \frac{N}{2} \{2[\alpha_{cc}^{vg}]^* c_{\theta}^2 + (\alpha_{aa}^{vg} + \alpha_{bb}^{vg})^* s_{\theta}^2\} \mu_c^{vg} c_{\theta} \\ &= N[\alpha_{cc}^{vg}]^* \mu_c^{vg} \{(1 - r_{vg}^*) c_{\theta}^2 + r_{vg}^*\} c_{\theta} \end{aligned} \quad (66)$$

with $2r_{vg} \equiv (\alpha_{aa}^{vg} + \alpha_{bb}^{vg})/\alpha_{cc}^{vg}$. More importantly, (65) directly gives

$$[\chi_{vg}^A]_{zzz} = N[\alpha_{cc}^{vg}]^* \{r_{vg}^* (R_{13}R_{13} + R_{23}R_{23}) + R_{33}R_{33}\} \mu_c^{vg} R_{33},$$

which results in the same expression as (66) on averaging over χ and ϕ . Below, we list the other elements for surface vibrational SFG analysis.

$$[\chi_{vg}^A]_{xxz} = \frac{N}{2} [\alpha_{cc}^{vg}]^* \mu_c^{vg} \{(r_{vg}^* - 1) c_{\theta}^2 + r_{vg}^* + 1\} c_{\theta} = [\chi_{vg}^A]_{yyz} \quad (67)$$

$$[\chi_{vg}^A]_{xzx} = \frac{N}{2} [\alpha_{cc}^{vg}]^* \mu_c^{vg} (1 - r_{vg}^*) s_{\theta}^2 c_{\theta} = [\chi_{vg}^A]_{yyz} = [\chi_{vg}^A]_{zxx} = [\chi_{vg}^A]_{zyy} \quad (68)$$

$$\begin{aligned}
[\chi_{vg}^A]_{xyz} &= [\chi_{vg}^A]_{xzy} = [\chi_{vg}^A]_{zxy} = 0 \quad (69) \\
[\chi_{vg}^{E_1}]_{zzz} &= \frac{N}{2}(\alpha_{ac}^{vg} + i\alpha_{bc}^{vg})^*(\mu_a^{vg} + i\mu_b^{vg})s_\theta^2 c_\theta \\
[\chi_{vg}^{E_1}]_{xxz} &= -\frac{N}{4}(\alpha_{ac}^{vg} + i\alpha_{bc}^{vg})^*(\mu_a^{vg} + i\mu_b^{vg})s_\theta^2 c_\theta = [\chi_{vg}^{E_1}]_{yyz} \\
[\chi_{vg}^{E_1}]_{xzx} &= \frac{N}{4}(\alpha_{ac}^{vg} + i\alpha_{bc}^{vg})^*(\mu_a^{vg} + i\mu_b^{vg})c_\theta^3 = [\chi_{vg}^{E_1}]_{zyz} \\
[\chi_{vg}^{E_1}]_{zxx} &= \frac{N}{4}(\alpha_{ac}^{vg} + i\alpha_{bc}^{vg})^*(\mu_a^{vg} + i\mu_b^{vg})c_\theta^3 = [\chi_{vg}^{E_1}]_{zyz} \\
[\chi_{vg}^{E_1}]_{xyz} &= -[\chi_{vg}^{E_1}]_{yxz} = 0 \quad (70) \\
[\chi_{vg}^{E_1}]_{xzy} &= -[\chi_{vg}^{E_1}]_{yzx} = [\chi_{vg}^{E_1}]_{zxy} = -[\chi_{vg}^{E_1}]_{zyx} \\
&= \frac{N}{8}i\{[\alpha_{ac}^{vg}]^*\mu_a^{vg} + [\alpha_{bc}^{vg}]^*\mu_b^{vg} + \\
&\quad i([\alpha_{ac}^{vg}]^*\mu_b^{vg} - [\alpha_{bc}^{vg}]^*\mu_a^{vg})\}(s_\theta^2 - 2c_\theta^2) \quad (71)
\end{aligned}$$

Calculations show that all the chiral tensor elements of (62)–(64) are zero for the A-species vibrations. So far no SFG peaks corresponding to the chiral elements of $\chi^{(2)}$ have been observed for molecules of C_{3v} symmetry. Therefore, it is reasonably assumed in the Appendix that

$$[\alpha_{ac}^{vg}]^*\mu_b^{vg} = [\alpha_{bc}^{vg}]^*\mu_a^{vg} \quad (72)$$

As far as α and μ are real, values of $[\alpha_{ji}^{vg}]^*\mu_k^{vg}$ are also real even for transitions of the degenerate E_1 -species vibrations, since phases from $q_r^{E_1}$ and $q_r^{E_1}$ cancel each other. Thus, if (72) is true for the α -helical molecules, the quantity in the right-hand side of (71) is a pure imaginary number that contributes nothing to the SFG intensities [see (56)].

V. Four-, Five-, and Six-Wave Mixing Spectroscopy

Typical vibrational four-wave mixing processes related to $\chi^{(3)}$ are shown in Figure 3b and Figure 3c, corresponding to $\alpha_{ij}^{gv}\alpha_{kl}^{vg}$ and $\beta_{ijk}^{gv}\mu_l^{vg}$, respectively. The related vibrational selection rules, as well as equations for molecular orientation relative to the sample surface, can easily be deduced from the calculated infrared, Raman, and TRHR tensors. The corresponding transition susceptibility tensor elements in the LF frame are found to be

$$[\chi_{vg}^\Gamma]_{ijkl} = N\{(\mathbf{R}\hat{i})^T[\alpha_{vg}^\Gamma]^\dagger(\mathbf{R}\hat{j})\}\{(\mathbf{R}\hat{k})^T[\alpha_{vg}^\Gamma]\mathbf{R}\hat{l}\} \quad (73)$$

$$[\chi_{vg}^\Gamma]_{ijkl} = N\{(\mathbf{R}\hat{j})^T[(\mathbf{R}\hat{i})^T\beta_{vg}^\Gamma]^\dagger(\mathbf{R}\hat{k})\}\{[\mu_{vg}^\Gamma]^T(\mathbf{R}\hat{l})\} \quad (74)$$

All the nonzero expressions of these relations will be reported elsewhere.⁴⁷ Below, as a feasibility study for the α -helical symmetry, we simply derive expressions for $[\chi_{vg}^{E_1}]_{xxxx}$, $[\chi_{vg}^{E_1}]_{xxyy}$, and $[\chi_{vg}^{E_1}]_{zzyy}$ on averaging over χ and ϕ .

(i) Raman plus anti-Stokes Raman process:

$$\begin{aligned}
[\chi_{vg}^{E_1}]_{xxxx} &= \frac{N}{4}|\alpha_{ac}^{vg}|^2 \\
&\quad + i\alpha_{bc}^{vg}|^2\left\{(\mathbf{R}\hat{1})^T\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & i \\ 1 & i & 0 \end{pmatrix}(\mathbf{R}\hat{1})\right\}\left\{(\mathbf{R}\hat{1})^T\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & -i \\ 1 & -i & 0 \end{pmatrix}(\mathbf{R}\hat{1})\right\}
\end{aligned}$$

$$= \frac{N}{4}|\alpha_{ac}^{vg}|^2 + i\alpha_{bc}^{vg}|^2(c_\theta^2 + 1)s_\theta^2 \quad (75)$$

$$[\chi_{vg}^{E_1}]_{xxyy} = -\frac{N}{4}|\alpha_{ac}^{vg}|^2 + i\alpha_{bc}^{vg}|^2s_\theta^4 \quad (76)$$

$$[\chi_{vg}^{E_1}]_{zzyy} = -\frac{N}{2}|\alpha_{ac}^{vg}|^2 + i\alpha_{bc}^{vg}|^2c_\theta^2s_\theta^2 \quad (77)$$

(ii) Infrared plus TRHR process:

$$\begin{aligned}
[\chi_{vg}^{E_1}]_{xxxx} &= N\{(\mathbf{R}\hat{1})^T(R_{11}[\beta_a^{E_1}]^{vg} + R_{21}[\beta_b^{E_1}]^{vg} + \\
&\quad R_{31}[\beta_c^{E_1}]^{vg})^\dagger(\mathbf{R}\hat{1})\}\{[\mu_{vg}^{E_1}]^T(\mathbf{R}\hat{1})\} \\
&= \frac{N}{64}\{2(\eta_{aaa}^{E_1})^{vg}(c_\theta^4 + 6c_\theta^2 + 1) + (2\eta_{aaa}^{E_1} + \eta_{bab}^{E_1} + \eta_{bba}^{E_1} + \\
&\quad i\eta_{aab}^{E_1} + i\eta_{aba}^{E_1})^{vg}s_\theta^4 + 4(\beta_{cca}^{vg} + \beta_{cac}^{vg} + \beta_{acc}^{vg} + i\beta_{ccb}^{vg} + \\
&\quad i\beta_{cbc}^{vg} + i\beta_{bcc}^{vg})(c_\theta^2 + 1)s_\theta^2\}^*(\mu_a^{vg} + i\mu_b^{vg}) \\
[\chi_{vg}^{E_1}]_{xxyy} &= N\{(\mathbf{R}\hat{1})^T(R_{11}[\beta_a^{E_1}]^{vg} + R_{21}[\beta_b^{E_1}]^{vg} + R_{31}[\beta_c^{E_1}]^{vg})^\dagger \\
&\quad (\mathbf{R}\hat{2})\}\{[\mu_{vg}^{E_1}]^T(\mathbf{R}\hat{2})\} \\
&= \frac{N}{64}\{(4\eta_{aaa}^{E_1} + \eta_{bba}^{E_1} + i\eta_{aab}^{E_1})^{vg}s_\theta^4 + (\eta_{bab}^{E_1} + i\eta_{aba}^{E_1})^{vg}(c_\theta^4 + \\
&\quad 6c_\theta^2 + 1) - 4(\beta_{cca}^{vg} + \beta_{acc}^{vg} + i\beta_{ccb}^{vg} + i\beta_{bcc}^{vg})s_\theta^4 + 4(\beta_{cac}^{vg} + \\
&\quad i\beta_{cbc}^{vg})(c_\theta^2 + 1)s_\theta^2\}^*(\mu_a^{vg} + i\mu_b^{vg}) \\
[\chi_{vg}^{E_1}]_{zzyy} &= N\{(\mathbf{R}\hat{3})^T(R_{13}[\beta_a^{E_1}]^{vg} + R_{23}[\beta_b^{E_1}]^{vg} + R_{33}[\beta_c^{E_1}]^{vg})^\dagger \\
&\quad (\mathbf{R}\hat{2})\}\{[\mu_{vg}^{E_1}]^T(\mathbf{R}\hat{2})\} \\
&= \frac{N}{32}\{(2\eta_{aaa}^{E_1} + \eta_{bab}^{E_1} + i\eta_{aba}^{E_1})^{vg}(c_\theta^2 + 1)s_\theta^2 + (2\eta_{aaa}^{E_1} + \\
&\quad \eta_{bba}^{E_1} + i\eta_{aab}^{E_1})^{vg}s_\theta^4 - 4(\beta_{cca}^{vg} + \beta_{acc}^{vg} + i\beta_{ccb}^{vg} + i\beta_{bcc}^{vg})c_\theta^2s_\theta^2 + \\
&\quad 4(\beta_{cac}^{vg} + i\beta_{cbc}^{vg})(c_\theta^2 + 1)c_\theta^2\}^*(\mu_a^{vg} + i\mu_b^{vg})
\end{aligned}$$

For the nonlinear optical processes of Figure 3, parts d, e, and f,⁶⁴ we may simply use the following expressions, respectively,

$$[\chi_{vg}^\Gamma]_{ijklm} = N\{(\mathbf{R}\hat{j})^T[(\mathbf{R}\hat{i})^T\beta_{vg}^\Gamma]^\dagger(\mathbf{R}\hat{k})\}\{(\mathbf{R}\hat{l})^T[\alpha_{vg}^\Gamma](\mathbf{R}\hat{m})\} \quad (78)$$

$$[\chi_{vg}^\Gamma]_{ijklm} = N\{(\mathbf{R}\hat{i})^T[\alpha_{vg}^\Gamma]^\dagger(\mathbf{R}\hat{j})\}\{(\mathbf{R}\hat{l})^T[(\mathbf{R}\hat{k})^T\beta_{vg}^\Gamma](\mathbf{R}\hat{m})\} \quad (79)$$

$$\begin{aligned}
[\chi_{vg}^\Gamma]_{ijklmn} &= \\
&\quad N\{(\mathbf{R}\hat{j})^T[(\mathbf{R}\hat{i})^T\beta_{vg}^\Gamma]^\dagger(\mathbf{R}\hat{k})\}\{(\mathbf{R}\hat{m})^T[(\mathbf{R}\hat{l})^T\beta_{vg}^\Gamma](\mathbf{R}\hat{n})\} \quad (80)
\end{aligned}$$

Computation of these elements is straightforward if we know the infrared, Raman, and HR tensors for any underlying molecular symmetries. The process of (80) has to include vibrations of E_3 -modes in addition to those of the A-, E_1 -, and E_2 -species. This shows clearly that it is convenient to deduce the relations of MF and LF tensors using the method described in this paper for higher order nonlinear spectroscopy.

VI. Concluding Remarks

The symmetries of a molecule are important in understanding its vibrational infrared and Raman activity. This is because vibrational modes of a molecule are classified into irreducible representations of the underlying molecular symmetry group, and projections of the molecular dipole moment and polarizability tensor to each irreducible species directly provide

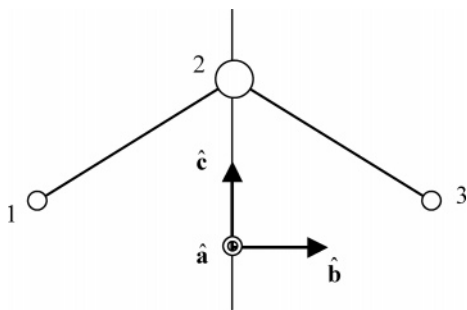


Figure 4. Definition of an MF coordinate frame for a molecule of C_{2v} symmetry.

selection rules for vibrational infrared and Raman spectroscopy, respectively.

In a similar way, for the α -helix as an example, we have explicitly computed all the nonzero TRHR tensors and deduced selection rules for TRHR spectroscopy, where vibrations of the E_3 -species are found to be active as well as those of the A_1 , E_1 , and E_2 -species. The computed infrared, Raman, and TRHR tensors are applied to deduce selection rules for SFG and four-wave mixing vibrational spectroscopy, as well as expressions for molecular orientation information, viz., the relations between MF tensors and nonzero elements of susceptibility tensors in a LF frame. Further details for four-wave mixing spectroscopy will be reported elsewhere. We also demonstrate the feasibility of applying a similar methodology to understand the five- and six-wave mixing vibrational transitions. This research provides a systematic way to analyze selection rules and relations between the MF hyperpolarizability and LF susceptibility tensors for nonlinear optical spectroscopy. The application of such methods to interpret physical measurements of α -helical structures will be reported in the future.

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Appendix

Since C_{2v} and C_{3v} are important molecular symmetry groups for nonlinear optical spectroscopy, we summarize their infrared, Raman, and TRHR tensors as well as the nonzero susceptibility tensor elements for surface vibrational SFG spectroscopy.

A1. C_{2v} Symmetry. There are four symmetry operations for a molecule of C_{2v} symmetry (like a water molecule): the identity transformation \mathbf{E} , a 2-fold rotation \mathbf{C}_2 about the c -axis, and two vertical planes of σ_v^{ca} (ca -plane) and σ_v^{cb} (cb -plane) [Figure 4]. In the MF coordinate frame, these can be represented by

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v^{ca} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_v^{cb} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

For the water molecule, there are only three genuine internal vibrations, where antisymmetric bond stretching vibrations belong to the B_2 -species while symmetric stretching and angle bending vibrations belong to the A_1 -species. By using the known character table for the C_{2v} group⁴⁸ and (17)–(19), the infrared, Raman, and hyper Raman tensors for its four irreducible

representations A_1 , A_2 , B_1 , and B_2 are listed in the following way.

(i) Infrared tensors:

$$\boldsymbol{\mu}^{A_1} = \frac{1}{4}\{\mathbf{E} + \mathbf{C}_2 + \sigma_v^{ca} + \sigma_v^{cb}\}\boldsymbol{\mu} = (0 \ 0 \ \mu_c)^T$$

$$\boldsymbol{\mu}^{A_2} = \frac{1}{4}\{\mathbf{E} + \mathbf{C}_2 - \sigma_v^{ca} - \sigma_v^{cb}\}\boldsymbol{\mu} = \mathbf{0}$$

$$\boldsymbol{\mu}^{B_1} = \frac{1}{4}\{\mathbf{E} - \mathbf{C}_2 + \sigma_v^{ca} - \sigma_v^{cb}\}\boldsymbol{\mu} = (\mu_a \ 0 \ 0)^T$$

$$\boldsymbol{\mu}^{B_2} = \frac{1}{4}\{\mathbf{E} - \mathbf{C}_2 - \sigma_v^{ca} + \sigma_v^{cb}\}\boldsymbol{\mu} = (0 \ \mu_b \ 0)^T$$

(ii) Raman tensors:

$$\boldsymbol{\alpha}^{A_1} = \begin{pmatrix} \alpha_{aa} & 0 & 0 \\ 0 & \alpha_{bb} & 0 \\ 0 & 0 & \alpha_{cc} \end{pmatrix} \quad \boldsymbol{\alpha}^{A_2} = \begin{pmatrix} 0 & \alpha_{ab} & 0 \\ \alpha_{ba} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\boldsymbol{\alpha}^{B_1} = \begin{pmatrix} 0 & 0 & \alpha_{ac} \\ 0 & 0 & 0 \\ \alpha_{ca} & 0 & 0 \end{pmatrix} \quad \boldsymbol{\alpha}^{B_2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{bc} \\ 0 & \alpha_{cb} & 0 \end{pmatrix}$$

(iii) TRHR tensors: Since $\{\mathbf{O}_g\boldsymbol{\beta}\}_c = \boldsymbol{\beta}_c$ for all $g \in C_{2v}$, $\boldsymbol{\beta}_c^\Gamma$ have the same form as $\boldsymbol{\alpha}^\Gamma$ for all irreducible representations Γ of C_{2v} , and we list only the TRHR tensors for $\boldsymbol{\beta}_a^\Gamma$ and $\boldsymbol{\beta}_b^\Gamma$ below.

$$\boldsymbol{\beta}_a^{A_1} = \begin{pmatrix} 0 & 0 & \beta_{aac} \\ 0 & 0 & 0 \\ \beta_{aca} & 0 & 0 \end{pmatrix} \quad \boldsymbol{\beta}_b^{A_1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \beta_{bbc} \\ 0 & \beta_{bcb} & 0 \end{pmatrix}$$

$$\boldsymbol{\beta}_a^{A_2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \beta_{abc} \\ 0 & \beta_{acb} & 0 \end{pmatrix} \quad \boldsymbol{\beta}_b^{A_2} = \begin{pmatrix} 0 & 0 & \beta_{bac} \\ 0 & 0 & 0 \\ \beta_{bca} & 0 & 0 \end{pmatrix}$$

$$\boldsymbol{\beta}_a^{B_1} = \begin{pmatrix} \beta_{aaa} & 0 & 0 \\ 0 & \beta_{abb} & 0 \\ 0 & 0 & \beta_{acc} \end{pmatrix} \quad \boldsymbol{\beta}_b^{B_1} = \begin{pmatrix} 0 & \beta_{bab} & 0 \\ \beta_{bba} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\boldsymbol{\beta}_a^{B_2} = \begin{pmatrix} 0 & \beta_{aab} & 0 \\ \beta_{aba} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \boldsymbol{\beta}_b^{B_2} = \begin{pmatrix} \beta_{baa} & 0 & 0 \\ 0 & \beta_{bbb} & 0 \\ 0 & 0 & \beta_{bcc} \end{pmatrix}$$

(iv) SFG: Susceptibility tensor elements after averaging over χ and ϕ : Since $\boldsymbol{\mu}^{A_2} = \mathbf{0}$, the A_2 -species modes make no contribution to observed vibrational SFG intensities. Calculations show that all the chiral tensor elements of (62)–(64) are zero for the A_1 -, B_1 -, and B_2 -species of C_{2v} . Since $\boldsymbol{\alpha}^T = \boldsymbol{\alpha}$, $\boldsymbol{\alpha}^{A_1}$ is essentially the same as $\boldsymbol{\alpha}^A$ of the α -helical symmetry, and expressions of $[\chi_{vg}^{A_1}]_{ijk}$ for surface vibrational SFG spectroscopy are the same as those for the α -helical symmetry [see (66)–(69)]. Below, we list only those for the other nonzero susceptibility tensor elements:

$$[\chi_{vg}^{B_1}]_{zzz} = N[\alpha_{ac}^{vg}]^* \mu_a^{vg} s_\theta^2 c_\theta$$

$$[\chi_{vg}^{B_1}]_{xxz} = -\frac{N}{2}[\alpha_{ac}^{vg}]^* \mu_a^{vg} s_\theta^2 c_\theta = [\chi_{vg}^{B_1}]_{yyz}$$

$$[\chi_{vg}^{B_1}]_{zxx} = \frac{N}{2}[\alpha_{ac}^{vg}]^* \mu_a^{vg} c_\theta^3 = [\chi_{vg}^{B_1}]_{lyz} = [\chi_{vg}^{B_1}]_{zxx} = [\chi_{vg}^{B_1}]_{zyy}$$

$$\begin{aligned}
[\chi_{vg}^{B_2}]_{zzz} &= N[\alpha_{bc}^{vg}]^* \mu_b^{vg} s_\theta^2 c_\theta \\
[\chi_{vg}^{B_2}]_{xxz} &= -\frac{N}{2}[\alpha_{ac}^{vg}]^* \mu_a^{vg} s_\theta^2 c_\theta = [\chi_{vg}^{B_2}]_{yyz} \\
[\chi_{vg}^{B_2}]_{xzx} &= \frac{N}{2}[\alpha_{bc}^{vg}]^* \mu_b^{vg} c_\theta^3 = [\chi_{vg}^{B_2}]_{zyz} = [\chi_{vg}^{B_2}]_{zxx} = [\chi_{vg}^{B_2}]_{zyy}
\end{aligned}$$

A2. C_{3v} Symmetry. There are six symmetry operations for a molecule of C_{3v} symmetry: the identity transformation \mathbf{E} , two 3-fold rotations \mathbf{C}_3 and \mathbf{C}_3^2 about the c -axis, and three vertical planes of σ_v^{1c} (containing the c -axis and atom 1), σ_v^{2c} (containing the c -axis and atom 2), and σ_v^{3c} (containing the c -axis and atom 3). If we define an MF frame as in Figure 5, these are represented in the basis of $\{\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\mathbf{c}}\}$ by

$$\begin{aligned}
\mathbf{E} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathbf{C}_3 &= \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \\
\sigma_v^{1c} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \sigma_v^{2c} &= \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ -\sqrt{3} & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \\
\sigma_v^{3c} &= \frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} & 0 \\ \sqrt{3} & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}
\end{aligned}$$

The symmetries of C_{3v} are classified into three irreducible species, A_1 , A_2 , and E (two-dimensional representation), whose character table can be found elsewhere.⁴⁸ Among the six genuine internal vibrations, the symmetric bond stretching and symmetric angle bending (or umbrella opening) vibrations belong to the A_1 -species, while the degenerate vibrations of asymmetric bond stretching and asymmetric angle bending belong to the E -species. Similarly, the infrared, Raman, TRHR tensors, and the nonzero susceptibility tensor elements for surface SFG spectroscopy can be listed in the following way.

(i) Infrared tensors:

$$\begin{aligned}
\boldsymbol{\mu}^{A_1} &= (0 \ 0 \ \mu_c)^T \\
\boldsymbol{\mu}^{A_2} &= \mathbf{0} \\
\boldsymbol{\mu}^E &= (\mu_a \ \mu_b \ 0)^T
\end{aligned}$$

(ii) Raman tensors:

$$\begin{aligned}
\boldsymbol{\alpha}^{A_1} &= \frac{1}{2} \begin{pmatrix} \alpha_{aa} + \alpha_{bb} & 0 & 0 \\ 0 & \alpha_{aa} + \alpha_{bb} & 0 \\ 0 & 0 & 2\alpha_{cc} \end{pmatrix} \\
\boldsymbol{\alpha}^{A_2} &= \frac{1}{2} \begin{pmatrix} 0 & \alpha_{ab} - \alpha_{ba} & 0 \\ \alpha_{ba} - \alpha_{ab} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
\boldsymbol{\alpha}^E &= \frac{1}{2} \begin{pmatrix} \alpha_{aa} - \alpha_{bb} & \alpha_{ab} + \alpha_{ba} & 2\alpha_{ac} \\ \alpha_{ba} + \alpha_{ab} & \alpha_{bb} - \alpha_{aa} & 2\alpha_{bc} \\ 2\alpha_{ca} & 2\alpha_{cb} & 0 \end{pmatrix}
\end{aligned}$$

Since $\alpha_{ij} = \alpha_{ji}$, α^{A_2} is found to be zero, we conclude that A_2 vibrations are also Raman inactive.

(iii) TRHR tensors: Since $\{\mathbf{O}_g \boldsymbol{\beta}\}_c = \boldsymbol{\beta}_c$ for all $g \in C_{3v}$, $\boldsymbol{\beta}_c^\Gamma$ have the same form as $\boldsymbol{\alpha}^\Gamma$ for all irreducible representations Γ

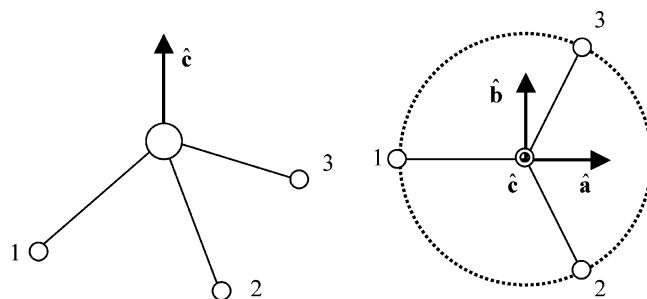


Figure 5. Definition of an MF coordinate frame for a molecule of C_{3v} symmetry.

of C_{3v} , and we list only the TRHR tensors for $\boldsymbol{\beta}_a^\Gamma$ and $\boldsymbol{\beta}_b^\Gamma$ below.

$$\begin{aligned}
\boldsymbol{\beta}_a^{A_1} &= \frac{1}{4} \begin{pmatrix} \beta_{aaa} - \beta_{abb} - \beta_{bab} - \beta_{bba} & 0 & 2(\beta_{aac} + \beta_{bbc}) \\ 0 & \beta_{abb} - \beta_{aaa} + \beta_{bab} + \beta_{bba} & 0 \\ 2(\beta_{aca} + \beta_{bcb}) & 0 & 0 \end{pmatrix} \\
\boldsymbol{\beta}_a^{A_2} &= \frac{1}{4} \begin{pmatrix} 0 & \beta_{bab} + \beta_{bba} - \beta_{aaa} + \beta_{abb} & 0 \\ \beta_{bba} + \beta_{bab} - \beta_{aaa} + \beta_{abb} & 0 & 2(\beta_{bbc} + \beta_{aac}) \\ 0 & 2(\beta_{bcb} + \beta_{aca}) & 0 \end{pmatrix} \\
\boldsymbol{\beta}_b^{A_1} &= \frac{1}{4} \begin{pmatrix} 0 & \beta_{aab} + \beta_{aba} + \beta_{baa} - \beta_{bbb} & 0 \\ \beta_{aba} + \beta_{aab} + \beta_{baa} - \beta_{bbb} & 0 & 2(\beta_{abc} + \beta_{bac}) \\ 0 & 2(\beta_{acb} + \beta_{bca}) & 0 \end{pmatrix} \\
\boldsymbol{\beta}_b^{A_2} &= \frac{1}{4} \begin{pmatrix} \beta_{baa} - \beta_{bbb} + \beta_{aab} + \beta_{aba} & 0 & 2(\beta_{bac} - \beta_{abc}) \\ 0 & \beta_{bbb} - \beta_{baa} - \beta_{aab} - \beta_{aba} & 0 \\ 2(\beta_{bca} - \beta_{acb}) & 0 & 0 \end{pmatrix} \\
\boldsymbol{\beta}_a^E &= \frac{1}{4} \begin{pmatrix} 3\beta_{aaa} + \beta_{abb} + \beta_{bab} + \beta_{bba} & 3\beta_{aab} - \beta_{aba} - \beta_{baa} + \beta_{bbb} & 2(\beta_{aac} - \beta_{bbc}) \\ 3\beta_{aba} - \beta_{aab} - \beta_{baa} + \beta_{bbb} & 3\beta_{abb} + \beta_{aaa} - \beta_{bab} - \beta_{bba} & 2(\beta_{abc} + \beta_{bac}) \\ 2(\beta_{aca} - \beta_{bcb}) & 2(\beta_{acb} + \beta_{bca}) & 4\beta_{acc} \end{pmatrix} \\
\boldsymbol{\beta}_b^E &= \frac{1}{4} \begin{pmatrix} 3\beta_{baa} + \beta_{bbb} - \beta_{aab} - \beta_{aba} & 3\beta_{bab} - \beta_{bba} + \beta_{aaa} - \beta_{abb} & 2(\beta_{bac} + \beta_{abc}) \\ 3\beta_{bba} - \beta_{bab} + \beta_{baa} - \beta_{abb} & 3\beta_{bbb} + \beta_{baa} + \beta_{aab} + \beta_{aba} & 2(\beta_{bbc} - \beta_{aac}) \\ 2(\beta_{bca} + \beta_{acb}) & 2(\beta_{bcb} - \beta_{aca}) & 4\beta_{bcc} \end{pmatrix}
\end{aligned}$$

(iv) SFG: Susceptibility tensor elements after averaging over χ and ϕ : Since $\boldsymbol{\mu}^{A_2} = \mathbf{0}$, observed vibrational SFG intensities for molecules of C_{3v} symmetry are only affected by modes belonging to the A_1 - or E -species. The SFG susceptibility tensor elements for the A_1 -species have the same expression as those of the C_{2v} group, since $\boldsymbol{\alpha}^T = \boldsymbol{\alpha}$. We list only susceptibility tensor elements for the E -species below:

$$\begin{aligned}
[\chi_{vg}^E]_{zzz} &= N\{[\alpha_{ac}^{vg}]^* \mu_a^{vg} + [\alpha_{bc}^{vg}]^* \mu_b^{vg}\} s_\theta^2 c_\theta \\
[\chi_{vg}^E]_{xxz} &= -\frac{N}{2}\{[\alpha_{ac}^{vg}]^* \mu_a^{vg} + [\alpha_{bc}^{vg}]^* \mu_b^{vg}\} s_\theta^2 c_\theta = [\chi_{vg}^E]_{yyz} \\
[\chi_{vg}^E]_{xzx} &= \frac{N}{2}\{[\alpha_{ac}^{vg}]^* \mu_a^{vg} + [\alpha_{bc}^{vg}]^* \mu_b^{vg}\} c_\theta^3 = [\chi_{vg}^E]_{zyz} = [\chi_{vg}^E]_{zyy} \\
[\chi_{vg}^E]_{xyx} &= -[\chi_{vg}^E]_{yxx} = 0 \\
[\chi_{vg}^E]_{lxy} &= \frac{N}{4}\{[\alpha_{ac}^{vg}]^* \mu_b^{vg} - [\alpha_{bc}^{vg}]^* \mu_a^{vg}\} (2c_\theta^2 - s_\theta^2) = \\
& -[\chi_{vg}^E]_{yxx} = [\chi_{vg}^E]_{zxy} = -[\chi_{vg}^E]_{zyx}
\end{aligned}$$

So far no vibrational SFG peaks corresponding to all the chiral tensor elements have been observed for molecules of C_{3v}

symmetry. This implicitly suggests that we have to assume (72), ensuring $[\chi_{vg}^E]_{xzy} = -[\chi_{vg}^E]_{lyz} = [\chi_{vg}^E]_{xxy} = -[\chi_{vg}^E]_{lyx} = 0$.

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