Theor Chem Account (2008) 119:39–55
DOI 10.1007/s00214-007-0267-9

REGULAR ARTICLE

Theory of Raman scattering and Raman optical activity: near resonance theory and levels of approximation

Laurence A. Nafie

Received: 20 May 2006 / Accepted: 13 February 2007 / Published online: 27 April 2007

Abstract A new level of the theory of Raman scattering and Raman optical activity (ROA) is identified between the general, unrestricted (GU) theory and the far-from-resonance (FFR) theory called the near resonance (NR) theory. In the NR theory, the Raman tensor is not symmetric, and there is nonequivalence between the incident and scattered circular polarization (ICP and SCP) forms of ROA and non-zero intensity for out-of-phase dual circular polarization ($\mathrm{DCP_{II}}$) ROA. Several levels of theory are identified in passing from the GU theory to the FFR theory. The NR theory provides vibronic detail, present in the GU theory but absent from the FFR, by assuming that the vibrational levels of the excited electronic states are the same as those of the ground electronic state. The NR theory obeys time-reversal symmetry and can be expressed in a form that is computationally tractable, thereby providing an improved description of the frequency dependence of Raman and ROA intensities relative to that provided by the FFR theory.

Keywords Raman scattering · Raman optical activity · Pre-resonance · Frequency dependence · Near resonance · Complete adiabatic · Nuclear velocity dependence

1 Introduction

Raman optical activity (ROA) is a form of natural optical activity that is distinct from the classical forms of optical activity, optical rotation and circular dichroism [1–3]. All forms of natural optical activity can be defined as the differential interaction of a chiral molecule with right versus left circularly polarized radiation. The most common form of ROA is vibrational ROA, although ROA in electronic Raman scattering can in principle be observed. Vibrational ROA is one of two forms of vibrational optical activity (VOA) [3–5]. The other is infrared or near-infrared vibrational circular dichroism, (VCD), which is the difference in the absorption of a molecule for left versus right circularly polarized radiation for a vibrational transition. VCD and ROA are complementary and nonredundant forms of VOA in the same way that infrared absorption and Raman scattering are complementary forms of ordinary vibrational spectroscopy.

Raman optical activity (ROA) was originally defined as the difference in Raman scattering intensity for right minus left *incident* circularly polarized (ICP) light [1,2]. The original formulation also included the possibility of observing ROA as the *degree of circularity* in the *scattered* light, but no explicit method of measurement of this form of ROA was proposed until it was measured as the intensity difference of circular polarization states in the scattered Raman radiation and renamed scattered circular polarization (SCP) ROA [6]. Subsequently, the definition and measurement of ROA was extended to include two new forms of ROA called *dual* circular polarization (DCPI and DCPII) ROA [7–9], and then further extended to include four forms of linear polarization (LP) ROA [10]. The four forms of CP ROA have been described in a complete theoretical formulation by means of two independent derivations [11], and all forms and experimental setups of CP and LP ROA have been described in a review starting from a single master equation [12].

L. A. Nafie (✉)
Department of Chemistry, Syracuse University,
Syracuse, NY, 13244-4100, USA
e-mail: lnafie@syr.edu

There are various theoretical expressions for ROA scattering tensors depending on the polarization modulation scheme, the scattering geometry and the proximity of the exciting laser radiation to resonance with excited electronic states in the molecule. A general unrestricted (GU) theory of ROA can be written from which all special cases can be derived [12]. The two principal resonance limits for the GU theory of ROA are the far-from-resonance (FFR) theory, the original form of the theory of ROA, and the single-electronic-state (SES) limit, for the case of strong resonance with a single excited electronic state [13]. In the case of FFR ROA, *ab initio* calculations have been carried out for direct comparison to experiment for two distinct cases, the zero frequency, static approximation for the incident radiation [14] and also, using time-dependent quantum perturbation methods, the FFR approximation with explicit dependence on the frequency of the incident radiation [15]. The SES approximation is so simple that the complete SES-ROA spectrum can be predicted from the parent resonance Raman spectrum and the electronic circular dichroism spectrum of the resonant electronic state [13].

The focus of this paper is on the transition from the GU theory of ROA to the FFR theory. The vibronic coupling formalism is introduced into the GU theory as a first step to separate the electronic and nuclear motions of the molecule. Then the approximations needed to reduce the GU theory to the standard FFR theory are invoked. The relative importance of these approximations is assessed and an intermediate level of the theory is identified that is not as severe as the FFR approximation. The new level of theory is called the near-resonance (NR) theory which becomes important as the FFR theory breaks down but before the regime of strong resonance with individual excited electronics state is reached. It is shown that the breakdown of the FFR approximation occurs only when excited-state vibronic detail becomes important. Symptoms of this breakdown, which have been observed experimentally in ROA experiments, are the loss of equivalence of ICP and SCP forms of ROA and the appearance of $\mathrm{DCP_{II}}$ ROA which vanishes in the FFR approximation [9,16].

The NR theory rests on the assumption that the vibrational structures of the most important excited electronic states are the same as those of the ground electronic state. This new level of Raman and ROA theory can be reduced to a comparatively simple form and it is shown that it provides an improved description of the frequency dependence of Raman and ROA intensities in the regime between the FFR approximation and the GU theory. Rather than having no vibronic detail in the energy denominators of the Raman and ROA tensor expressions, the NR theory of Raman and ROA includes vibronic detail under the assumption that, to a reasonable approximation, the vibrational structure of the contributing excited electronic states is the same as that of the ground electronic state. While this is not true in general, it is a better assumption than simply removing all vibronic detail and ignoring the difference in frequency between the incident and scattered radiation. As a result, in addition to agreeing with experiment for the appearance of non-zero $\mathrm{DCP_{II}}$ ROA and differences between ICP and SCP ROA for molecules that are *not* close to *strong* resonance by ten or more thousands of wavenumbers, the NR theory provides a more accurate description of the frequency dependence of both Raman and ROA spectra as resonance with the excited states of the molecule is approached. Finally, it is shown that the NR theory reduces to a simple form that is straightforward to calculate at the *ab initio* level given a program that includes the frequency dependence of Raman and ROA on the incident laser radiation.

2 Polarized light scattering

The intensity of light scattering for any experiment can be expressed in terms of the general scattering tensor $\tilde{a}_{\alpha\beta}$ and the polarization vectors for the incident and scattered radiation, $\tilde{e}^i_\alpha$ and $\tilde{e}^d_\alpha$, respectively, and is given by

$$I\left(\tilde{e}^d, \tilde{e}^i\right) = 90K\left\langle \left| \tilde{e}^{d*}_\alpha \tilde{a}_{\alpha\beta} \tilde{e}^i_\beta \right|^2 \right\rangle \tag{1}$$

In this equation, K is a constant given below that depends among other things on the intensity of the incident laser radiation. The angular brackets designate an average over all angles of orientation of the molecule to the laboratory frame of reference. This is needed for liquid, solution or gaseous samples where there are no unique molecular axes relative to the laboratory axes. The polarization vectors have one Greek subscript and the scattering tensor has two. For repeated Greek subscripts, summation over the Cartesian directions x, y and z is implied. Hence, Eq. (1) has nine terms within the vertical brackets, and these brackets designate the absolute value of the complex quantities within the brackets. The tilde above a quantity, such as a polarization vector or a scattering tensor, indicates that this quantity can be complex. The star superscript for the polarization vector of the scattered light designates complex conjugation. The constant K is given by

$$K = \frac{1}{90}\left(\frac{\omega_s^2 \mu_0 \tilde{E}^{(0)}}{4\pi R}\right)^2 \tag{2}$$

where ω_s is the angular frequency of the scattered light, μ_0 is the magnetic permeability of free space, $\tilde{E}^{(0)}$ is the effective electric field strength of the incident laser radiation of angular frequency ω_0, and R is the distance from the scattering to the detector. The general scattering tensor is given through its lowest-order tensors as

$$\tilde{a}_{\alpha\beta} = \tilde{\alpha}_{\alpha\beta} + \frac{1}{c}\left[\varepsilon_{\gamma\delta\beta} n^i_\delta \tilde{G}_{\alpha\gamma} + \varepsilon_{\gamma\delta\alpha} n^d_\delta \tilde{\mathscr{G}}_{\gamma\beta} + \frac{i}{3}\left(\omega_0 n^i_\gamma \tilde{A}_{\alpha,\gamma\beta} - \omega_s n^d_\gamma \tilde{\mathscr{A}}_{\beta,\gamma\alpha}\right)\right] \quad (3)$$

where the first tensor is simply the polarizability tensor that is responsible for ordinary Raman (and Rayleigh) scattering. The four tensors in square brackets are the optical activity tensors or in the case of ROA, the ROA tensors. The first two are magnetic dipole-electric dipole ROA tensors and the second two are electric quadrupole-electric dipole ROA tensors. The vectors $\tilde{n}^i_\alpha$ and $\tilde{n}^d_\alpha$ are the propagation vectors for the incident and scattered light, respectively, and $\varepsilon_{\alpha\beta\gamma}$ is the unit antisymmetric tensor that is +1 for even permutations of the order x,y,z, -1 for odd permutation of this order, and zero if any two Cartesian directions are the same. We note that three additional terms may be added to Eq. (3) to account for electric field induced birefringence and the effects of finite cone of collection of the Raman scattering and ROA [3].

The Raman polarizability tensor is given by

$$\tilde{\alpha}_{\alpha\beta} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|n\rangle}{\omega_{jn} - \omega_0 - i\Gamma_j} + \frac{\langle m|\hat{\mu}_\beta|j\rangle\langle j|\hat{\mu}_\alpha|n\rangle}{\omega_{jm} + \omega_0 + i\Gamma_j}\right] \quad (4)$$

where $\hbar$ is Planck's constant divided by 2π, and the summation is over all excited electronic states, j, except the initial and final states, n and m, respectively. The states n and m differ by a vibrational quantum of energy. The denominators contain frequency terms, and ω_{jn} is the angular frequency difference between the states j and n. The terms $i\Gamma_j$ are imaginary terms proportional to the width of the electronic state j, and hence inversely proportional to its lifetime. We have followed the opposite-sign convention for the $i\Gamma_j$ terms recognized recently to be the correct one based on a number of physical and phenomenological arguments [17–19]. The first term in Eq. (4) is called the resonance term since difference between the jn-transition frequency and the laser frequency vanishes at the resonance condition, and the second term is the non-resonance term. The quantities in angular brackets are quantum mechanical matrix elements with electric dipole moment operators $\hat{\mu}_\alpha$ given by

$$\hat{\mu}_\alpha = \sum_k e_k r_{k\alpha} \quad (5)$$

which is simply the summation over the charge and position in the α^{th} direction of all particles, k, in the molecule, electrons and nuclei, although in the case of Raman scattering or ROA the nuclei make no contributions.

The matrix element in Eq. (4) involving the operator $\hat{\mu}_\beta$ describes the interaction of the molecule with the incident radiation while the matrix elements with the operator $\hat{\mu}_\alpha$ describes the interaction of the molecule with the scattered radiation. The matrix element products in each term can be read from right to left in a time-ordered sense, and hence the resonance term describes the molecule interacting first with a laser photon and subsequently creating a scattered photon, whereas the non-resonance terms reverses the time-order of the those two events.

The four ROA tensors differ from the Raman polarizability tensor by substitution of a higher-order operator for an electric-dipole operator in Eq. (4). The two operators needed for ROA are the magnetic-dipole moment operator and the electric-quadruple moment operator given respectively by

$$\hat{m}_\alpha = \frac{1}{2}\sum_k \frac{e_k}{m_k}\varepsilon_{\alpha\beta\gamma} r_{k\beta} p_{k\gamma} \quad (6)$$

$$\hat{\Theta}_{\alpha\beta} = \frac{1}{2}\sum_k e_k\left(3r_{k\alpha}r_{k\beta} - r_k^2\delta_{\alpha\beta}\right) \quad (7)$$

The resulting ROA tensors are given by

$$\tilde{G}_{\alpha\beta} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{\mu}_\alpha|j\rangle\langle j|\hat{m}_\beta|n\rangle}{\omega_{jn} - \omega_0 - i\Gamma_j} + \frac{\langle m|\hat{m}_\beta|j\rangle\langle j|\hat{\mu}_\alpha|n\rangle}{\omega_{jm} + \omega_0 + i\Gamma_j}\right] \quad (8)$$

$$\tilde{\mathscr{G}}_{\alpha\beta} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{m}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|n\rangle}{\omega_{jn} - \omega_0 - i\Gamma_j} + \frac{\langle m|\hat{\mu}_\beta|j\rangle\langle j|\hat{m}_\alpha|n\rangle}{\omega_{jm} + \omega_0 + i\Gamma_j}\right] \quad (9)$$

$$\tilde{A}_{\alpha,\beta\gamma} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\Theta}_{\beta\gamma}|n\rangle}{\omega_{jn} - \omega_0 - i\Gamma_j} + \frac{\langle m|\hat{\Theta}_{\beta\gamma}|j\rangle\langle j|\hat{\mu}_\alpha|n\rangle}{\omega_{jm} + \omega_0 + i\Gamma_j}\right] \quad (10)$$

$$\tilde{\mathscr{A}}_{\alpha,\beta\gamma} = \frac{1}{\hbar}\sum_{j\neq m,n}\left[\frac{\langle m|\hat{\Theta}_{\beta\gamma}|j\rangle\langle j|\hat{\mu}_\alpha|n\rangle}{\omega_{jn} - \omega_0 - i\Gamma_j} + \frac{\langle m|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\Theta}_{\beta\gamma}|n\rangle}{\omega_{jm} + \omega_0 + i\Gamma_j}\right] \quad (11)$$

The expressions given above provide the theoretical formalism for the description of all forms of polarized Raman scattering through first-order in the magnetic-dipole and electric-quadrupole interaction of light with matter. This is sufficient to describe the various forms of ROA within the assumptions given above.

3 ROA observables

If the polarization states of the incident laser radiation and the scattered radiation are specified, one can construct theoretical expressions for the various ROA observables that can be measured. Considering here only circular polarization ROA, expressions can be obtained from pairs of intensity expressions that differ only in the change in the circular polarization state of one or both the light beams from right circular to left circular, or vice versa.

The fundamental ROA observables are classified by polarization and scattering angle, ξ.

There are four different forms of CP ROA given by

$$\text{ICP ROA:} \quad \Delta I_\alpha(\xi) = I_\alpha^R(\xi) - I_\alpha^L(\xi) \tag{12}$$

$$\text{SCP ROA:} \quad \Delta I^\alpha(\xi) = I_R^\alpha(\xi) - I_L^\alpha(\xi) \tag{13}$$

$$\text{DCP}_\text{I}\text{ROA:} \quad \Delta I_I(\xi) = I_R^R(\xi) - I_L^L(\xi) \tag{14}$$

$$\text{DCP}_\text{II}\text{ROA:} \quad \Delta I_{II}(\xi) = I_L^R(\xi) - I_R^L(\xi) \tag{15}$$

In the case of ICP and SCP ROA, the polarization state α is any fixed linear value or the unpolarized state. The standard choices are unpolarized, linearly polarized parallel to the scattering plane (depolarized) or linearly polarized perpendicular to the scattering plane (polarized). The common scattering angles are 90° (right-angle scattering) 180° (backscattering), and 0° (forward scattering).

4 General unrestricted theory of ROA

The GU theory of ROA embraces all possible polarization experiments, scattering geometries and degrees of resonance Raman intensity enhancement. Because of this generality, the level of the theory is too complex to describe in detail in the present context. Instead, we provide a verbal description of the formalism and refer the interested reader to a comprehensive review by Nafie and Che, 1994, of the theory and measurement of ROA [12].

ROA and Raman intensity are proportional to the square of a tensor quantity, as expressed in Eq. (1). For Raman scattering, only the square of the polarizability is needed, whereas ROA intensity arises from the products of the polarizability and the ROA tensors. The ROA tensors are approximately three orders of magnitude smaller than the polarizability, and hence an ROA spectrum is approximately three orders of magnitude smaller than its parent Raman spectrum. As noted above, the Greek subscripts of the tensors refer to the molecular axis system. However, for both Raman and ROA, linear combinations of products of tensors can be found that do not vary with the choice of the molecular coordinate frame. Such combinations are called invariants. All Raman intensities from samples of randomly oriented molecules can be expressed in terms of only three invariants, called the isotropic Raman invariant and the symmetric and antisymmetric anisotropic Raman invariants given by

$$\alpha^2 = \frac{1}{9}\,\mathrm{Re}\left[(\tilde{\alpha}_{\alpha\alpha})^S \left(\tilde{\alpha}_{\beta\beta}\right)^{S^*}\right] \tag{16}$$

$$\beta_S(\tilde{\alpha})^2 = \frac{1}{2}\,\mathrm{Re}\left[3\left(\tilde{\alpha}_{\alpha\beta}\right)^S \left(\tilde{\alpha}_{\alpha\beta}\right)^{S^*} - (\tilde{\alpha}_{\alpha\alpha})^S \left(\tilde{\alpha}_{\beta\beta}\right)^{S^*}\right] \tag{17}$$

$$\beta_A(\tilde{\alpha})^2 = \frac{1}{2}\,\mathrm{Re}\left[3\left(\tilde{\alpha}_{\alpha\beta}\right)^A \left(\tilde{\alpha}_{\alpha\beta}\right)^{A^*}\right] \tag{18}$$

where the symmetric and anti-symmetric forms of the tensors here and below are given by

$$\left(T_{\alpha\beta}\right)^S = \frac{1}{2}\left[\left(T_{\alpha\beta}\right) + \left(T_{\beta\alpha}\right)\right] \tag{19}$$

$$\left(T_{\alpha\beta}\right)^A = \frac{1}{2}\left[\left(T_{\alpha\beta}\right) - \left(T_{\beta\alpha}\right)\right] \tag{20}$$

For CP ROA there are ten invariants, five associated with the Roman tensors, $\Big(\alpha G, \beta_S\left(\tilde{G}\right)^2, \beta_A\left(\tilde{G}\right)^2, \beta_S\left(\tilde{A}\right)^2$ and $\beta_A\left(\tilde{A}\right)^2\Big)$ and five with the script tensors, $(\alpha\mathscr{G}$, $\beta_S\left(\tilde{\mathscr{G}}\right)^2, \beta_A\left(\tilde{\mathscr{G}}\right)^2, \beta_S\left(\tilde{\mathscr{A}}\right)^2$ and $\beta_A\left(\tilde{\mathscr{A}}\right)^2\Big)$. The Roman ROA tensors are given by

$$\alpha G = \frac{1}{9}\,\mathrm{Im}\left[(\tilde{\alpha}_{\alpha\alpha})^S \left(\tilde{G}_{\beta\beta}\right)^{S^*}\right] \tag{21}$$

$$\beta_S\left(\tilde{G}\right)^2 = \frac{1}{2}\,\mathrm{Im}\left[3(\tilde{\alpha}_{\alpha\beta})^S \left(\tilde{G}_{\alpha\beta}\right)^{S^*} - (\tilde{\alpha}_{\alpha\alpha})^S \left(\tilde{G}_{\beta\beta}\right)^{S^*}\right] \tag{22}$$

$$\beta_A\left(\tilde{G}\right)^2 = \frac{1}{2}\,\mathrm{Im}\left[3(\tilde{\alpha}_{\alpha\beta})^A \left(\tilde{G}_{\alpha\beta}\right)^{A^*}\right] \tag{23}$$

$$\beta_S\left(\tilde{A}\right)^2 = \frac{1}{2}\omega_0\,\mathrm{Im}\left\{i(\tilde{\alpha}_{\alpha\beta})^S \left[\varepsilon_{\alpha\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)\right]^{S^*}\right\} \tag{24}$$

$$\beta_A\left(\tilde{A}\right)^2 = \frac{1}{2}\omega_0\,\mathrm{Im}\left\{i(\tilde{\alpha}_{\alpha\beta})^A \left\{\left[\varepsilon_{\alpha\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)\right]^{A^*} + \left[\varepsilon_{\alpha\beta\gamma}\left(\tilde{A}_{\delta,\gamma\delta}\right)\right]^{A^*}\right\}\right\} \tag{25}$$

The corresponding five script tensor invariants are the same as those for the Roman tensors, except that ω_s replaces ω_0 in the expressions for the electric quadrupole optical activity invariants. . All of the different CP ROA experiments can be expressed in terms of these ten invariants. The ROA intensity for any experiment is expressed as a linear combination of some or all of the ten ROA invariants. Although sets of experiments can be devised to isolate all three ordinary Raman invariants, only six distinct combinations of ROA invariants can be isolated [12].

From an experimental point of view, the most important ROA experiments are unpolarized backscattering ICP and SCP, and $\mathrm{DCP_I}$. The expressions for the circular intensity difference (ROA) and circular intensity sum (Raman) for these experiments are:
ICP (180°):

$$I_u^R(180°)-I_u^L(180°) = \frac{8K}{c}\Big[45\alpha G+7\beta_S\big(\tilde{G}\big)^2 +5\beta_A\big(\tilde{G}\big)^2+\beta_S\big(\tilde{A}\big)^2-\beta_A\big(\tilde{A}\big)^2 +45\alpha\mathscr{G}-5\beta_S\big(\tilde{\mathscr{G}}\big)^2+5\beta_A\big(\tilde{\mathscr{G}}\big)^2 +3\beta_S\big(\tilde{\mathscr{A}}\big)^2-\beta_A\big(\tilde{\mathscr{A}}\big)^2\Big] \tag{26}$$

$$I_u^R(180°)+I_u^L(180°) = 4K\Big[45\alpha^2+7\beta_S(\tilde{\alpha})^2+5\beta_A(\tilde{\alpha})^2\Big] \tag{27}$$

SCP (180°):

$$I_L^u(180°)-I_R^u(180°) = \frac{8K}{c}\Big[-45\alpha G+5\beta_S\big(\tilde{G}\big)^2 -5\beta_A\big(\tilde{G}\big)^2+3\beta_S\big(\tilde{A}\big)^2+\beta_A\big(\tilde{A}\big)^2 -45\alpha\mathscr{G}-7\beta_S\big(\tilde{\mathscr{G}}\big)^2-5\beta_A\big(\tilde{\mathscr{G}}\big)^2 +\beta_S\big(\tilde{\mathscr{A}}\big)^2+\beta_A\big(\tilde{\mathscr{A}}\big)^2\Big] \tag{28}$$

$$I_R^u(180°)+I_L^u(180°) = 4K\Big[45\alpha^2+7\beta_S(\tilde{\alpha})^2+5\beta_A(\tilde{\alpha})^2\Big] \tag{29}$$

$\mathrm{DCP_I}(180°)$:

$$I_R^R(180°)-I_R^L(180°) = \frac{8K}{c}\Big[6\beta_S\big(\tilde{G}\big)^2+2\beta_S\big(\tilde{A}\big)^2 -6\beta_S\big(\tilde{\mathscr{G}}\big)^2+2\beta_S\big(\tilde{\mathscr{A}}\big)^2\Big] \tag{30}$$

$$I_R^R(180°)+I_L^L(180°) = 4K\Big[6\beta_S(\tilde{\alpha})^2\Big] \tag{31}$$

Both ICP (180°) and SCP (180°) Raman and ROA experiments use all available invariants and the ROA are different from one another. By contrast, the extra circular polarization discrimination gives $\mathrm{DCP_I}(180°)$ Raman and ROA a remarkable level of simplicity. Only the symmetric anisotropic invariants contribute. $\mathrm{DCP_{II}}(180°)$ intensities are obtained by subtracting intensities for $\mathrm{DCP_I}(180°)$ from those for ICP (180°) or SCP (180°), although in the case of SCP (180°) ROA, the $\mathrm{DCP_{II}}(180°)$ ROA is obtained with the opposite sign from the definition given in Eq. (15).

5 Far-from-resonance theory of ROA

The transition from the general theory to the FFR theory starts with invoking the adiabatic approximation to separate the molecular wavefunction into the product of electronic and vibrational parts. Without loss of significant generality, we also restrict the Raman vibrational transition to be a Stokes transition between the zeroth and first vibrational levels of normal mode *a* of the ground electronic state. With these changes to the polarizability in Eq. (4), one obtains

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\left[\frac{\left\langle\phi^a_{g1}\left|\langle g\left|\hat{\mu}_\alpha\right|e\rangle\right|\phi_{ev}\right\rangle\left\langle\phi_{ev}\left|\langle e\left|\hat{\mu}_\beta\right|g\rangle\right|\phi^a_{g0}\right\rangle}{\omega_{ev,g0}-\omega_0-i\Gamma_e} + \frac{\left\langle\phi^a_{g1}\left|\langle g\left|\hat{\mu}_\beta\right|e\rangle\right|\phi_{ev}\right\rangle\left\langle\phi_{ev}\left|\langle e\left|\hat{\mu}_\alpha\right|g\rangle\right|\phi^a_{g0}\right\rangle}{\omega_{ev,g1}+\omega_0+i\Gamma_e}\right] \tag{32}$$

To reduce this expression to the FFR approximation several steps typically occur. The imaginary damping terms are dropped as small compared to the real frequency terms and all excited-state vibronic detail is dropped from the energy denominators. These two types of omission are each on the order of 1,000 cm^{-1} and can be considered small relative to the resonance mismatch, which can be on the order of tens of thousands of wavenumbers. An alternative form of the denominator of the nonresonance term $\omega_{ev,g1}+\omega_0+i\Gamma_e$ is $\omega_{ev,g0}+\omega_s+i\Gamma_e$ where is ω_s the frequency of the Raman scattered light, and where elimination of vibrational detail in the denominators of Eq. (32) also eliminates the discrimination between the incident and scattered radiation frequencies. Without vibrational detail in the denominators, the sum over the excited state vibrational wavefunctions can be carried out to closure leaving the initial and final vibrational sublevels of the ground electronic state as the only vibrational wavefunctions. These can be separated from the polarizability to give

$$\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} = \left\langle\phi^a_{g1}\right|\frac{1}{\hbar}\sum_{e}\left[\frac{\langle g|\hat{\mu}_a|e\rangle\langle e|\hat{\mu}_\beta|g\rangle}{\omega^0_{eg}-\omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle\langle e|\hat{\mu}_a|g\rangle}{\omega^0_{eg}+\omega_0}\right]\left|\phi^a_{g0}\right\rangle \tag{33}$$

From the Hermitian properties of the position dipole moment operator we can write

$$\begin{aligned}\langle g|\hat{\mu}_\beta|e\rangle\langle e|\hat{\mu}_a|g\rangle &= \langle g|\hat{\mu}_a|e\rangle^*\langle e|\hat{\mu}_\beta|g\rangle^* \\ &= \langle g|\hat{\mu}_a|e\rangle\langle e|\hat{\mu}_\beta|g\rangle\end{aligned} \tag{34}$$

and Eq. (33) can then be combined over a common denominator as [3]

$$\begin{aligned}(\tilde{\alpha}_{\alpha\beta})^{a}_{g1,g0} &= \left\langle \phi^{a}_{g1} \right| \alpha_{\alpha\beta} \left| \phi^{a}_{g0} \right\rangle \\ &= \left\langle \phi^{a}_{g1} \right| \frac{2}{\hbar}\,\mathrm{Re}\sum_{e\neq g} \frac{\omega^{0}_{eg}\langle g|\hat{\mu}_{\alpha}|e\rangle\langle e|\hat{\mu}_{\beta}|g\rangle}{\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}} \left| \phi^{a}_{g0} \right\rangle\end{aligned} \tag{35}$$

Invoking the same approximations for the ROA tensors the following expressions are obtained

$$\begin{aligned}\left(G'_{\alpha\beta}\right)^{a}_{g0,g1} &= \left\langle \phi^{a}_{g1} \right| G'_{\alpha\beta} \left| \phi^{a}_{g0} \right\rangle \\ &= -\left\langle \phi^{a}_{g1} \right| \frac{2}{\hbar}\,\mathrm{Im}\sum_{e\neq g} \frac{\omega_{0}\langle g|\hat{\mu}_{\alpha}|e\rangle\langle e|\hat{m}_{\beta}|g\rangle}{\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}} \left| \phi^{a}_{g0} \right\rangle\end{aligned} \tag{36}$$

$$\begin{aligned}\left(\mathscr{G}'_{\alpha\beta}\right)^{a}_{g0,g1} &= \left\langle \phi^{a}_{g1} \right| \mathscr{G}'_{\alpha\beta} \left| \phi^{a}_{g0} \right\rangle \\ &= -\left\langle \phi^{a}_{g1} \right| \frac{2}{\hbar}\,\mathrm{Im}\sum_{e\neq g} \frac{\omega_{0}\langle g|\hat{m}_{\alpha}|e\rangle\langle e|\hat{\mu}_{\beta}|g\rangle}{\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}} \left| \phi^{a}_{g0} \right\rangle\end{aligned} \tag{37}$$

$$\begin{aligned}(A_{\alpha,\beta\gamma})^{a}_{g0,g1} &= \left\langle \phi^{a}_{g1} \right| A_{\alpha,\beta\gamma} \left| \phi^{a}_{g0} \right\rangle \\ &= \left\langle \phi^{a}_{g1} \right| \frac{2}{\hbar}\,\mathrm{Re}\sum_{e\neq g} \frac{\omega^{0}_{eg}\langle g|\hat{\mu}_{\alpha}|e\rangle\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle}{\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}} \left| \phi^{a}_{g0} \right\rangle\end{aligned} \tag{38}$$

$$\begin{aligned}(\mathscr{A}_{\alpha,\beta\gamma})^{a}_{g0,g1} &= \left\langle \phi^{a}_{g1} \right| \mathscr{A}_{\alpha,\beta\gamma} \left| \phi^{a}_{g0} \right\rangle \\ &= \left\langle \phi^{a}_{g1} \right| \frac{2}{\hbar}\,\mathrm{Re}\sum_{e\neq g} \frac{\omega^{0}_{eg}\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle\langle e|\hat{\mu}_{\alpha}|g\rangle}{\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}} \left| \phi^{a}_{g0} \right\rangle\end{aligned} \tag{39}$$

where, we have used the Hermitian properties of the imaginary magnetic-dipole and the real electric-quadrupole operators,

$$\begin{aligned}\left\langle g\middle|\widehat{m}_{\beta}\middle|e\right\rangle\langle e|\hat{\mu}_{\alpha}|g\rangle &= \langle g|\hat{\mu}_{\alpha}|e\rangle^{*}\left\langle e\middle|\widehat{m}_{\beta}\middle|g\right\rangle^{*} \\ &= -\langle g|\hat{\mu}_{\alpha}|e\rangle\left\langle e\middle|\widehat{m}_{\beta}\middle|g\right\rangle\end{aligned} \tag{40}$$

$$\begin{aligned}\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle\langle e|\hat{\mu}_{\alpha}|g\rangle &= \langle g|\hat{\mu}_{\alpha}|e\rangle^{*}\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle^{*} \\ &= \langle g|\hat{\mu}_{\alpha}|e\rangle\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle\end{aligned} \tag{41}$$

in the expressions for the ROA tensors analogous to Eq. (33). The primed and unprimed tensors arise from the following definition of the complex tensor.

$$\tilde{T} = T - iT' \tag{42}$$

Finally, we form the symmetric and anti-symmetric combinations of these tensors. The Raman polarizability in Eq. (33) with Eq. (34) is symmetric, and hence

$$\left[(\alpha_{\alpha\beta})^{a}_{g1,g0}\right]^{S} = \frac{1}{2}\left[(\alpha_{\alpha\beta})^{a}_{g1,g0} + (\alpha_{\beta\alpha})^{a}_{g1,g0}\right] \tag{43}$$

$$\left[(\alpha_{\alpha\beta})^{a}_{g1,g0}\right]^{A} = \frac{1}{2}\left[(\alpha_{\alpha\beta})^{a}_{g1,g0} - (\alpha_{\beta\alpha})^{a}_{g1,g0}\right] = 0 \tag{44}$$

As a result, the anti-symmetric Raman and ROA invariants in Eqs. (18), (23) and (25) vanish. We now need only consider the symmetric combinations of the ROA tensors, and using the relations in Eqs. (40) and (41), we obtain

$$\begin{aligned}\left[\left(G'_{\alpha\beta}\right)^{a}_{g1,g0}\right]^{S} &= \frac{1}{2}\left[\left(G'_{\alpha\beta}\right)^{a}_{g1,g0} + \left(G'_{\beta\alpha}\right)^{a}_{g1,g0}\right] \\ &= -\left[\left(\mathscr{G}'_{\alpha\beta}\right)^{a}_{g1,g0}\right]^{S}\end{aligned} \tag{45}$$

$$\begin{aligned}\left[\varepsilon_{\alpha\gamma\delta}\left(A_{\gamma,\delta\beta}\right)^{a}_{g1,g0}\right]^{S} &= \frac{1}{2}\left[\varepsilon_{\alpha\gamma\delta}\left(A_{\gamma,\delta\beta}\right)^{a}_{g1,g0}\right. \\ &\qquad \left. + \varepsilon_{\beta\gamma\delta}\left(A_{\gamma,\delta\alpha}\right)^{a}_{g1,g0}\right] \\ &= \left[\varepsilon_{\alpha\gamma\delta}\left(\mathscr{A}_{\gamma,\delta\beta}\right)^{a}_{g1,g0}\right]^{S}\end{aligned} \tag{46}$$

From the expressions above, the theory of ROA simplifies dramatically. In particular, all five anti-symmetric Raman and ROA invariants vanish as the result of Eq. (44).

$$\beta_{A}(\tilde{\alpha})^{2}, \beta_{A}\left(\tilde{G}\right)^{2}, \beta_{A}\left(\tilde{A}\right)^{2}, \beta_{A}\left(\tilde{\mathscr{G}}\right)^{2}, \beta_{A}\left(\tilde{\mathscr{A}}\right)^{2} = 0 \tag{47}$$

And there is no need to use the subscript for symmetric and anti-symmetric tensors combinations as for the polarizability invariant

$$\left[\beta_{S}(\alpha)^{2}\right]^{a}_{g1,g0} = \left[\beta(\alpha)^{2}\right]^{a}_{g1,g0} \tag{48}$$

Further, from Eqs. (45) and (46), the six symmetric ROA invariants reduce to three

$$[\alpha G]^{a}_{g1,g0} = -[\alpha\mathscr{G}]^{a}_{g1,g0} = \left[\alpha G'\right]^{a}_{g1,g0} \tag{49}$$

$$\left[\beta_{S}\left(\tilde{G}\right)^{2}\right]^{a}_{g1,g0} = -\left[\beta_{S}\left(\tilde{\mathscr{G}}\right)^{2}\right]^{a}_{g1,g0} = \left[\beta\left(G'\right)^{2}\right]^{a}_{g1,g0} \tag{50}$$

$$\left[\beta_{S}\left(\tilde{A}\right)^{2}\right]^{a}_{g1,g0} = \left[\beta_{S}\left(\tilde{\mathscr{A}}\right)^{2}\right]^{a}_{g1,g0} = \left[\beta(A)^{2}\right]^{a}_{g1,g0} \tag{51}$$

The equations for the two Raman invariants and three ROA invariants are

$$\left[\alpha^2\right]^a_{g1,g0} = \frac{1}{9}(\alpha_{\alpha\alpha})^a_{g1,g0}(\alpha_{\beta\beta})^a_{g1,g0} \tag{52}$$

$$\left[\beta(\alpha)^2\right]^a_{g1,g0} = \frac{1}{2}\left[3(\alpha_{\alpha\beta})^a_{g1,g0}(\alpha_{\alpha\beta})^a_{g1,g0} - (\alpha_{\alpha\alpha})^a_{g1,g0}(\alpha_{\beta\beta})^a_{g1,g0}\right] \tag{53}$$

$$\left[\alpha G'\right]^a_{g1,g0} = \frac{1}{9}(\alpha_{\alpha\alpha})^a_{g1,g0}\left(G'_{\beta\beta}\right)^a_{g1,g0} \tag{54}$$

$$\left[\beta(G')^2\right]^a_{g1,g0} = \frac{1}{2}\left[3(\alpha_{\alpha\beta})^a_{g1,g0}\left(G'_{\alpha\beta}\right)^a_{g1,g0} - (\alpha_{\alpha\alpha})^a_{g1,g0}\left(G'_{\beta\beta}\right)^a_{g1,g0}\right] \tag{55}$$

$$\left[\beta(A)^2\right]^a_{g1,g0} = \frac{1}{2}\omega_0(\alpha_{\alpha\beta})^a_{g1,g0}\varepsilon_{\alpha\gamma\delta}(A_{\gamma,\delta\beta})^a_{g1,g0} \tag{56}$$

and the FFR polarizability and optical activity tensors are given by

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{e\neq g}\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2 - \omega_0^2}\,\mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle\right] \tag{57}$$

$$G'_{\alpha\beta} = \frac{-2}{\hbar}\sum_{e\neq g}\frac{\omega_0}{\left(\omega^0_{eg}\right)^2 - \omega_0^2}\,\mathrm{Im}\left[\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{m}_\beta|g\rangle\right] \tag{58}$$

$$A_{\alpha,\beta\gamma} = \frac{2}{\hbar}\sum_{e\neq g}\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2 - \omega_0^2}\,\mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle\left\langle e\left|\hat{\Theta}_{\beta\gamma}\right|g\right\rangle\right] \tag{59}$$

At this level of approximation the difference between ICP and SCP ROA vanishes, as does differences between ICP/SCP ROA and DCP$_\mathrm{I}$ ROA. The analogs of Eqs. (26) through (32) are given by:

ICP(180°) = SCP(180°):

$$I^R_u(180°) - I^L_u(180°) = \frac{8K}{c}\left\{12\left[\beta(G')^2\right]^a_{g1,g0} + 4\left[\beta(A)^2\right]^a_{g1,g0}\right\} \tag{60}$$

$$I^R_u(180°) + I^L_u(180°) = 4K\left\{45\left[\alpha^2\right]^a_{g1,g0} + 7\left[\beta(\alpha)^2\right]^a_{g1,g0}\right\} \tag{61}$$

DCP$_\mathrm{I}$ (180°):

$$I^R_R(180°) - I^L_R(180°) = \frac{8K}{c}\left\{12\left[\beta(G')^2\right]^a_{g1,g0} + 4\left[\beta(A)^2\right]^a_{g1,g0}\right\} \tag{62}$$

$$I^R_R(180°) + I^L_R(180°) = 4K\left\{6\left[\beta(\alpha)^2\right]^a_{g1,g0}\right\} \tag{63}$$

In order to evaluate the tensor invariants in Eqs. (52)–(56) for the vibrational transition from $g0$ to $g1$ in harmonic approximation, derivatives of the tensors with respect to normal coordinates are needed. We use the following notation for this purpose

$$\left[\alpha^2\right]^a_{g1,g0} = \frac{1}{9}\left\langle\phi^a_{g1}|\alpha_{\alpha\alpha}|\phi^a_{g0}\right\rangle\left\langle\phi^a_{g1}|\alpha_{\beta\beta}|\phi^a_{g0}\right\rangle \tag{64}$$

$$\left\langle\phi^a_{g1}|\alpha_{\alpha\alpha}|\phi^a_{g0}\right\rangle = \left(\frac{\partial\alpha_{\alpha\alpha}}{\partial Q_a}\right)_0\left\langle\phi^a_{g1}|Q_a|\phi^a_{g0}\right\rangle + \ldots \tag{65}$$

$$\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a}\right)_0 = \frac{2}{\hbar}\sum_{e\neq g}\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right) - \omega_0^2} \times \mathrm{Re}\left[\left(\frac{\partial\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle}{\partial Q_a}\right)_0\right] \tag{66}$$

$$\left(\frac{\partial\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle}{\partial Q_a}\right)_0 = \langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0\langle e|\hat{\mu}_\beta|g\rangle + \langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0 \tag{67}$$

$$\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0 = \left(\frac{\partial\langle g|\hat{\mu}_\alpha|e\rangle}{\partial Q_a}\right)_0 = \left\langle\left(\frac{\partial\psi_g}{\partial Q_a}\right)_0|\hat{\mu}_\alpha\,|\,\psi_{e,0}\right\rangle + \left\langle\psi_{g,0}\,|\,\hat{\mu}_\alpha|\left(\frac{\partial\psi_e}{\partial Q_a}\right)_0\right\rangle \tag{68}$$

Using this notation at the level of the harmonic approximation, the Raman polarizability tensor in the FFR approximation in Eq. (33) is given by

$$(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_e\left[\frac{\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg} - \omega_0} + \frac{\langle e|\hat{\mu}_\alpha|g\rangle_0\langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0}{\omega^0_{eg} - \omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg} + \omega_0} + \frac{\langle e|\hat{\mu}_\beta|g\rangle_0\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0}{\omega^0_{eg} + \omega_0}\right]\left\langle\phi^a_{g1}|Q_\alpha|\phi^a_{g0}\right\rangle \tag{69}$$

6 Near resonance theory of Raman scattering

Starting again from the GU theory, we rewrite Eq. (32) for the Raman polarizability for a Stokes transition from $g0$ to $g1$ in vibrational mode a with the vibronic wavefunctions written as product wavefunctions.

$$(\tilde{\alpha}_{\alpha\beta})^a_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\left[\frac{\left\langle\phi^a_{g1}\,|\langle g|\hat{\mu}_\alpha|e\rangle\,|\phi_{ev}\rangle\,|\langle e|\hat{\mu}_\beta|g\rangle\,|\phi^a_{g0}\right\rangle}{\omega_{ev,g0} - \omega_0} + \frac{\left\langle\phi^a_{g1}\,|\langle g\,|\hat{\mu}_\beta|\,e\rangle\,|\phi_{ev}\rangle\,\langle\phi_{ev}|\,\langle e\,|\hat{\mu}_\alpha|\,g\rangle\,|\phi^a_{g0}\right\rangle}{\omega_{ev,g0} + \omega_0 - \omega_a}\right. \tag{70}$$

where we have used the relation that $\omega_{ev,g1} + \omega_0 = \omega_{ev,g0} + \omega_0 - \omega_a$ and ω_a is the frequency of the α^{th} vibrational mode. We have also dropped the imaginary terms since the resonance energy denominator is not expected to approach zero in the NR regime. The approximation made to reach the FFR theory is to replace $\omega_{ev,g0}$ by ω^0_{eg} and to ignore ω_a in the non-resonance term.

The NR Raman theory begins with the assumption that the excited state vibrational wavefunctions can be written as equivalent to a corresponding ground electronic state vibrational wavefunction for each normal mode a as $|\phi_{ev}\rangle = \left|\phi^a_{gv}\right\rangle$. Using this relation with the notation established in Eqs. (64)–(68) for the nuclear position dependence of the electronic matrix elements to first order in the nuclear normal coordinate Q_a yields

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_{ev}\Bigg[& \frac{\left\langle \phi^a_{g1} \right| \langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0 Q_a \left| \phi^a_{gv} \right\rangle \left\langle \phi^a_{gv} \right| \langle e|\hat{\mu}_\beta|g\rangle_0 \left| \phi^a_{g0} \right\rangle}{\omega_{ev,g0} - \omega_0} \\
& + \frac{\left\langle \phi^a_{g1} \right| \langle g|\hat{\mu}_\alpha|e\rangle_0 \left| \phi^a_{gv} \right\rangle \left\langle \phi^a_{gv} \right| \langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0 Q_a \left| \phi^a_{g0} \right\rangle}{\omega_{ev,g0} - \omega_0} \\
& + \frac{\left\langle \phi^a_{g1} \right| \langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0 Q_a \left| \phi^a_{gv} \right\rangle \left\langle \phi^a_{gv} \right| \langle e|\hat{\mu}_\alpha|g\rangle_0 \left| \phi^a_{g0} \right\rangle}{\omega_{ev,g0} + \omega_0 - \omega_a} \\
& + \frac{\left\langle \phi^a_{g1} \right| \langle g|\hat{\mu}_\beta|e\rangle_0 \left| \phi^a_{gv} \right\rangle \left\langle \phi^a_{gv} \right| \langle e|\hat{\mu}_\alpha|g\rangle^{Q_a}_0 Q_a \left| \phi^a_{g0} \right\rangle}{\omega_{ev,g0} + \omega_0 - \omega_a} \Bigg]
\end{aligned}
\tag{71}
$$

The sum over the vibrational wavefunction ϕ^a_{gv} can be carried out where, assuming harmonic oscillator selection rules, only the functions ϕ^a_{g0} or ϕ^a_{g1} contribute to the sum depending on the term being evaluated. The value of ν affects the energy denominator through $\omega_{ev,g0}$ since $\omega_{e0,g0} = \omega^0_{eg}$ and $\omega_{e1,g0} = \omega^0_{eg} + \omega_a$. Carrying out the sum over ν, evaluating the energy denominators, and rearranging the terms yields

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg[& \Bigg(\frac{\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0 \langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg} - \omega_0} \\
& + \frac{\langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0 \langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg} + \omega_0 - \omega_a} \Bigg) \\
& \times \left\langle \phi^a_{g1} \right| Q_a \left| \phi^a_{g0} \right\rangle \left\langle \phi^a_{g0} \middle| \phi^a_{g0} \right\rangle \\
& + \Bigg(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0}{\omega^0_{eg} + \omega_a - \omega_0} \\
& + \frac{\langle g|\hat{\mu}_\beta|e\rangle_0 \langle e|\hat{\mu}_\alpha|g\rangle^{Q_a}_0}{\omega^0_{eg} + \omega_0} \Bigg) \\
& \times \left\langle \phi^a_{g1} \middle| \phi^a_{g1} \right\rangle \left\langle \phi^a_{g1} \right| Q_a \left| \phi^a_{g0} \right\rangle \Bigg]
\end{aligned}
\tag{72}
$$

Using the normalization of the vibrational wavefunctions, one obtains

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_{e\neq g} & \Bigg(\frac{\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0 \langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg} - \omega_0} \\
& + \frac{\langle g|\hat{\mu}_\beta|e\rangle_0 \langle e|\hat{\mu}_\alpha|g\rangle^{Q_a}_0}{\omega^0_{eg} + \omega_0} \Bigg) \\
& + \Bigg(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0}{\omega^0_{eg} - \omega_s} \\
& + \frac{\langle g|\hat{\mu}_\beta|e\rangle^{Q_a}_0 \langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg} + \omega_s} \Bigg) \\
& \times \left\langle \phi^a_{g1} \right| Q_a \left| \phi^a_{g0} \right\rangle
\end{aligned}
\tag{73}
$$

where the Stokes Raman scattered frequency is given by $\omega_s = \omega_0 - \omega_a$. The FFR approximation for this equation, given in Eq. (69), is obtained from Eq. (73) by eliminating the vibrational frequency dependence from the denominator which now can be done simply by the approximation that $\omega_s = \omega_0$. Equation (73) takes into account that pre-resonance or resonance in Raman scattering is not just resonance with the *incident* laser radiation, but equally, by symmetry, with the *scattered* radiation. The pre-resonance frequency dependence correlates the frequency of the photon represented by the unperturbed electronic matrix element. In the first two terms, both resonance and non-resonance terms, this matrix element is the matrix element for the operator $\hat{\mu}_\beta$ associated with the incident radiation and here the photon frequency dependence is that of the incident radiation. For the second pair of terms, the unperturbed matrix element is the matrix element associated with $\hat{\mu}_\alpha$ for the scattered radiation, and in these terms the pre-resonance frequency dependence follows the scattered radiation frequency which varies in value across the Raman spectrum.

Using relationships of the form analogous to Eq. (34), we can write

$$
\langle g|\hat{\mu}_\beta|e\rangle^{Q_a *}_0 \langle e|\hat{\mu}_\alpha|g\rangle^*_0 = \langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0 \tag{74}
$$

and the first and second terms and the third and fourth terms in Eq. (73) can be combined over a common denominator to give

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{Q_a}_{g1,g0} = \frac{2}{\hbar}\sum_{e\neq g} & \Bigg[\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2 - \omega^2_0} \operatorname{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle^{Q_a}_0 \langle e|\hat{\mu}_\beta|g\rangle_0\right] \\
& \frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2 - \omega^2_s} \operatorname{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle^{Q_a}_0\right] \Bigg] \\
& \times \left\langle \phi^a_{g1} \right| Q_a \left| \phi^a_{g0} \right\rangle
\end{aligned}
\tag{75}
$$

The symmetry of the Raman tensor with respect to interchange of á and â, present in the FFR theory, has been lost in the NR theory due to the difference in the energy denominators for the third and fourth terms in Eq. (73) compared to the first and second terms, or the second term of Eq. (75) compared with the first. This asymmetry should occur whenever resonance is sufficiently close that the difference in the resonance felt by the incident and scattered radiation is numerically significant. Note that the deviation from symmetry can be expressed as a correction term, for the third and fourth terms in Eq. (70) by writing the photon frequency for these terms as

$$\omega_{eg}^{0} \pm (\omega_0 - \omega_a) = \omega_{eg}^{0} \pm \omega_0 (1 - \omega_a/\omega_0) \tag{76}$$

Ignoring the correction term ω_a/ω_0 restores the FFR theory. It is clear that the FFR theory becomes an ever better approximation as the vibrational frequency decreases and becomes exact in the limit of zero vibrational frequency or Rayleigh scattering.

7 Near resonance theory of ROA

Given the asymmetry in the Raman polarizability tensor with respect to interchange of α and β, the antisymmetric tensor invariant, $\left[(\alpha_{\alpha\beta})_{g1,g0}^{a}\right]^{A}$, which is zero in the FFR approximation, now becomes non-zero in the NR approximation with a magnitude on the order of the ratio of the vibrational frequency to that of the exciting radiation as illustrated in Eq. (73). In analogy to Eq. (72), the expressions for the Raman optical activity tensors in the NR approximation are given by

$$\begin{aligned}(\tilde{G}_{\alpha\beta})_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg(&\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{m}_\beta|g\rangle_0}{\omega_{eg}^{0}-\omega_0} \\ &+\frac{\langle g|\hat{m}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^{0}+\omega_0} \\ &+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{m}_\beta|g\rangle_0^{Q_a}}{\omega_{eg}^{0}-\omega_s} \\ &+\frac{\langle g|\hat{m}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^{0}+\omega_s}\Bigg)\left\langle\phi_{g1}^{a}|Q_a|\phi_{g0}^{a}\right\rangle\end{aligned} \tag{77}$$

$$\begin{aligned}(\tilde{\mathscr{G}}_{\alpha\beta})_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg(&\frac{\langle g|\hat{m}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega_{eg}^{0}-\omega_0} \\ &+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{m}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^{0}+\omega_0} \\ &+\frac{\langle g|\hat{m}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega_{eg}^{0}-\omega_s} \\ &+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{m}_\alpha|g\rangle}{\omega_{eg}^{0}+\omega_s}\Bigg)\left\langle\phi_{g1}^{a}|Q_a|\phi_{g0}^{a}\right\rangle\end{aligned} \tag{78}$$

$$\begin{aligned}(\tilde{A}_{\alpha,\beta\gamma})_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg(&\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle_0}{\omega_{eg}^{0}-\omega_0} \\ &+\frac{\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^{0}+\omega_0} \\ &+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle_0^{Q_a}}{\omega_{eg}^{0}-\omega_s} \\ &+\frac{\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^{0}+\omega_s}\Bigg)\left\langle\phi_{g1}^{a}|Q_a|\phi_{g0}^{a}\right\rangle\end{aligned} \tag{79}$$

$$\begin{aligned}\left(\tilde{\mathscr{A}}_{\alpha,\beta\gamma}\right)_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg(&\frac{\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^{0}-\omega_0} \\ &+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle_0^{Q_a}}{\omega_{eg}^{0}+\omega_0} \\ &+\frac{\left\langle g\middle|\hat{\Theta}_{\beta\gamma}\middle|e\right\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega_{eg}^{0}-\omega_s} \\ &+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\left\langle e\middle|\hat{\Theta}_{\beta\gamma}\middle|g\right\rangle_0}{\omega_{eg}^{0}+\omega_s}\Bigg)\left\langle\phi_{g1}^{a}|Q_a|\phi_{g0}^{a}\right\rangle\end{aligned} \tag{80}$$

Using the Hermitian properties of the matrix elements, as before, and combining terms over common denominators, we can write

$$\begin{aligned}\left(\tilde{G}_{\alpha\beta}\right)_{g1,g0}^{Q_a} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg[&\frac{\omega_0}{\left(\omega_{eg}^{0}\right)^2-\omega_0^2} \\ &\times \mathrm{Im}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{m}_\beta|g\rangle_0\right] \\ &+\frac{\omega_s}{\left(\omega_{eg}^{0}\right)^2-\omega_s^2}\,\mathrm{Im}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{m}_\beta|g\rangle_0^{Q_a}\right]\Bigg] \\ &\times\left\langle\phi_{g1}^{a}|Q_a|\phi_{g0}^{a}\right\rangle\end{aligned} \tag{81}$$

$$\begin{aligned}\left(\mathscr{G}'_{\alpha\beta}\right)^{Q_a}_{g1,g0} &= \frac{1}{\hbar}\sum_{e\neq g}\left[\frac{\omega_0}{\left(\omega^0_{eg}\right)^2-\omega_0^2}\right.\\ &\quad\times \mathrm{Im}\left[\langle g|\hat{m}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0\right]\\ &\quad\left.+\frac{\omega_s}{\left(\omega^0_{eg}\right)^2-\omega_s^2}\,\mathrm{Im}\left[\langle g|\hat{m}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}\right]\right]\\ &\quad\times\left\langle\phi^a_{g1}|Q_a|\phi^a_{g0}\right\rangle \qquad (82)\end{aligned}$$

$$\begin{aligned}\left(A_{\alpha,\beta\gamma}\right)^{Q_a}_{g1,g0} &= \frac{1}{\hbar}\sum_{e\neq g}\left[\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2-\omega_0^2}\right.\\ &\quad\times \mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\left\langle e\left|\hat{\Theta}_{\beta\gamma}\right|g\right\rangle_0\right]\\ &\quad\left.+\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2-\omega_s^2}\,\mathrm{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0\left\langle e\left|\hat{\Theta}_{\beta\gamma}\right|g\right\rangle_0^{Q_a}\right]\right]\\ &\quad\times\left\langle\phi^a_{g1}|Q_a|\phi^a_{g0}\right\rangle \qquad (83)\end{aligned}$$

$$\begin{aligned}\left(\mathscr{A}_{\alpha,\beta\gamma}\right)^{Q_a}_{g1,g0} &= \frac{1}{\hbar}\sum_{e\neq g}\left[\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2-\omega_0^2}\right.\\ &\quad\times \mathrm{Re}\left[\left\langle g\left|\hat{\Theta}_{\beta\gamma}\right|e\right\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0\right]\\ &\quad\left.+\frac{\omega^0_{eg}}{\left(\omega^0_{eg}\right)^2-\omega_s^2}\,\mathrm{Re}\left[\left\langle g\left|\hat{\Theta}_{\beta\gamma}\right|e\right\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}\right]\right]\\ &\quad\times\left\langle\phi^a_{g1}|Q_a|\phi^a_{g0}\right\rangle \qquad (84)\end{aligned}$$

For these expressions, the presence of ω_s instead of ω_0, as found in the FFR approximation, prevents the relationships that equate the Roman ROA tensors, or their invariants, to within a sign of the corresponding script ROA tensors, or their invariants, as in Eqs. (45) or (46). This permits differences, for example, between ICP-ROA and SCP-ROA even for the cases of symmetric invariants. Adding the antisymmetric invariants further differentiates these two forms of ROA.

8 Complete adiabatic theory of Raman scattering and ROA

We describe here a second way in which the FFR theory breaks down and gives rise to asymmetry in the Raman tensor. If the theory of Raman scattering and ROA is extended beyond Born-Oppenheimer approximation, there is also a loss of symmetry in the Raman tensor, as has been pointed out previously [20,21], and differences in the Roman and script ROA tensors and invariants. We begin by writing the complete adiabatic (CA) electronic wavefunction as a function of both the nuclear position and the nuclear velocity as [22,23]

$$\tilde{\psi}^{CA}_g(Q_a,P_a)=\psi_{g,0}+\left(\frac{\partial\tilde{\psi}_g}{\partial Q_a}\right)_{0,0}Q_a+\left(\frac{\partial\tilde{\psi}_g}{\partial P_a}\right)_{0,0}P_a+\cdots \qquad (85)$$

where in general the CA electronic wavefunction is complex and the double zero subscript refers to evaluation of the wavefunction at the equilibrium nuclear position and zero nuclear velocity. For convenience, we have chosen normal coordinates and conjugate momenta to express the nuclear dependence, but Cartesian coordinates could be used if desired. In terms of vibronic coupling, the CA wavefunction can be written as

$$\tilde{\psi}^{CA}_g(Q_a,P_a)=\psi_{g,0}+\sum_{s\neq g}C^a_{sg,0}\psi_{s,0}\left(Q_a+iP_a/\omega^0_{sg}\right)+\cdots \qquad (86)$$

Where the vibronic coupling matrix element is defined as

$$C^a_{sg,0}=\left\langle\psi_{s,0}\left|\left(\partial\psi_g/\partial Q_a\right)_0\right.\right\rangle \qquad (87)$$

From this equation it is clear that the nuclear position dependence represented by Q_a is real whereas the nuclear velocity dependence represented by P_a is pure imaginary. Substitution of Eq. (85) in Eq. (33) for the polarizability in the FFR approximation and using the notation

$$\begin{aligned}\langle g|\hat{\mu}_\alpha|e\rangle_0^{P_a} &= \left(\frac{\partial\langle g|\hat{\mu}_\alpha|e\rangle}{\partial P_a}\right)_0\\ &= \left\langle\left(\frac{\partial\tilde{\Psi}_g}{\partial P_a}\right)_0\left|\hat{\mu}_\alpha\right|\Psi_{e,0}\right\rangle\left\langle\Psi_{g,0}\right|\hat{\mu}_\alpha\left|\left(\frac{\partial\tilde{\Psi}_e}{\partial P_a}\right)_0\right\rangle \qquad (88)\end{aligned}$$

gives the full normal coordinate dependence of the polarizability tensor as

$$\begin{aligned}\left(\tilde{\alpha}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0} &= \frac{1}{\hbar}\sum_{e\neq g}\left\{\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg}-\omega_0}\right.\right.\\ &\quad+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega^0_{eg}+\omega_0}+\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega^0_{eg}-\omega_0}\\ &\quad\left.+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg}+\omega_0}\right)\left\langle\phi^a_{g1}\left|Q_a\right|\phi^a_{g0}\right\rangle\\ &\quad+\left(\frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{P_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg}-\omega_0}+\frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{P_a}}{\omega^0_{eg}+\omega_0}\right.\end{aligned}$$

$$
+ \frac{\langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle_0^{P_a}}{\omega_{eg}^0 - \omega_0} + \frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{P_a} \langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega_{eg}^0 + \omega_0} \Bigg)
\left\langle \phi_{g1}^a \,|P_a\, \middle|\phi_{g0}^a \right\rangle \Bigg\} \tag{89}
$$

In view of Eq. (86), relationships of the form

$$
\langle g|\hat{\mu}_\beta|e\rangle_0^{P_a^*} \langle e|\hat{\mu}_\alpha|g\rangle_0^* = - \langle g|\hat{\mu}_\alpha|e\rangle_0 \langle e|\hat{\mu}_\beta|g\rangle_0^{P_a} \tag{90}
$$

Similar terms can be collected over a common denominator as

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^a = {} & \frac{2}{\hbar} \sum_e \frac{\omega_{eg}^0 \operatorname{Re}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\beta|g\rangle_0 + \langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a} \langle e|\hat{\mu}_\alpha|g\rangle_0\right]}{\left(\omega_{eg}^0\right)^2 - \omega_0^2} \\
& \times \left\langle \phi_{g1}^a \,|Q_a\, \middle|\phi_{g0}^a \right\rangle \\
& + \frac{2}{\hbar} \sum_e \frac{\omega_0 \operatorname{Im}\left[\langle g|\hat{\mu}_\alpha|e\rangle_0^{P_a} \langle e|\hat{\mu}_\beta|g\rangle_0 + \langle g|\hat{\mu}_\beta|e\rangle_0^{P_a} \langle e|\hat{\mu}_\alpha|g\rangle_0\right]}{\left(\omega_{eg}^0\right)^2 - \omega_0^2} \\
& \times \left\langle \phi_{g1}^a \,|P_a\, \middle|\phi_{g0}^a \right\rangle
\end{aligned} \tag{91}
$$

The expression that depends on Q_a is symmetric with respect to interchange of subscripts α and β and can be deduced from FFR limit of the NR expression for the polarizability in Eq. (75). By contrast the expression that depends on P $a$is antisymmetric with respect to α and β interchange. In order to assess the relative magnitude of these terms, we substitute into Eq. (89) the CA electronic wavefunctions into the derivatives of the electronic matrix elements using the notation of Eqs. (68) and (88) and then (85) and (86) to obtain

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a,P_a} = {} & \frac{1}{\hbar} \sum_{e \neq g} \Bigg\{ \Bigg(\frac{C_{sg,0}^a \left(\hat{\mu}_\alpha\right)_{se,0} \left(\hat{\mu}_\beta\right)_{eg,0}}{\omega_{eg}^0 - \omega_0} \\
& + \frac{C_{sg,0}^a \left(\hat{\mu}_\beta\right)_{se,0} \left(\hat{\mu}_\alpha\right)_{eg,0}}{\omega_{eg}^0 + \omega_0} \Bigg) \\
& \times \left\langle \phi_{g1} \middle| \left(Q_a - iP_a/\omega_{sg}^0\right) \middle| \phi_{g0} \right\rangle \\
& + \Bigg(\frac{\left(\hat{\mu}_\alpha\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\beta\right)_{eg,0}}{\omega_{eg}^0 - \omega_0} \\
& + \frac{\left(\hat{\mu}_\beta\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\alpha\right)_{eg,0}}{\omega_{eg}^0 + \omega_0} \Bigg) \\
& \times \left\langle \phi_{g1} \middle| \left(Q_a + iP_a/\omega_{se}^0\right) \middle| \phi_{g0} \right\rangle \\
& + \Bigg(\frac{\left(\hat{\mu}_\alpha\right)_{ge,0} C_{se,0}^a \left(\hat{\mu}_\beta\right)_{sg,0}}{\omega_{eg}^0 - \omega_0} \\
& + \frac{\left(\hat{\mu}_\beta\right)_{ge,0} C_{se,0}^a \left(\hat{\mu}_\alpha\right)_{sg,0}}{\omega_{eg}^0 + \omega_0} \Bigg) \\
& \times \left\langle \phi_{g1} \middle| \left(Q_a - iP_a/\omega_{se}^0\right) \middle| \phi_{g0} \right\rangle \\
& + \Bigg(\frac{\left(\hat{\mu}_\alpha\right)_{ge,0} \left(\hat{\mu}_\beta\right)_{es,0} C_{sg,0}^a}{\omega_{eg}^0 - \omega_0} \\
& + \frac{\left(\hat{\mu}_\beta\right)_{ge,0} \left(\hat{\mu}_\alpha\right)_{es,0} C_{sg,0}^a}{\omega_{eg}^0 + \omega_0} \Bigg) \\
& \left\langle \phi_{g1} \middle| \left(Q_a + iP_a/\omega_{sg}^0\right) \middle| \phi_{g0} \right\rangle
\end{aligned} \tag{92}
$$

Using symmetry relations that hold for the electric dipole matrix elements of the form

$$
\left(\hat{\mu}_\beta\right)_{ge,0} \left(\hat{\mu}_\alpha\right)_{es,0} C_{sg,0}^a = C_{sg,0}^a \left(\hat{\mu}_\alpha\right)_{se,0} \left(\hat{\mu}_\beta\right)_{eg,0} \tag{93}
$$

we can combine terms over a common denominator and separate those terms that depend on Q_a from those that depend on P_a which yields

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a,P_a} = {} & \frac{1}{\hbar} \sum_{s,e \neq g} \Bigg\{ \omega_{eg}^0 \Bigg[\frac{C_{sg,0}^a \left(\hat{\mu}_\alpha\right)_{se,0} \left(\hat{\mu}_\beta\right)_{eg,0} + C_{sg,0}^a \left(\hat{\mu}_\beta\right)_{se,0} \left(\hat{\mu}_\alpha\right)_{eg,0}}{\left(\omega_{eg}^0\right)^2 - \omega_0^2} \\
& + \frac{\left(\hat{\mu}_\alpha\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\beta\right)_{eg,0} + \left(\hat{\mu}_\beta\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\alpha\right)_{eg,0}}{\left(\omega_{eg}^0\right)^2 - \omega_0^2} \Bigg] \\
& \times \left\langle \phi_{g1} \,|Q_a\, |\phi_{g0} \right\rangle \\
& - i\omega_0 \Bigg[\frac{C_{sg,0}^a \left(\hat{\mu}_\alpha\right)_{se,0} \left(\hat{\mu}_\beta\right)_{eg,0} - C_{sg,0}^a \left(\hat{\mu}_\beta\right)_{se,0} \left(\hat{\mu}_\alpha\right)_{eg,0}}{\omega_{sg}^0 \left[\left(\omega_{eg}^0\right)^2 - \omega_0^2\right]} \\
& - \frac{\left(\hat{\mu}_\alpha\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\beta\right)_{eg,0} - \left(\hat{\mu}_\beta\right)_{gs,0} C_{se,0}^a \left(\hat{\mu}_\alpha\right)_{eg,0}}{\omega_{se}^0 \left[\left(\omega_{eg}^0\right)^2 - \omega_0^2\right]} \Bigg] \\
& \times \left\langle \phi_{g1} \,|P_a\, |\phi_{g0} \right\rangle \Bigg\}
\end{aligned} \tag{94}
$$

Again, we find from Eq. (94) that the terms with Q_a-dependence are symmetric with $\alpha\beta$ interchange and those with P_a-dependence are correspondingly antisymmetric. These expressions can be related to earlier definitions of the symmetric and antisymmetric parts of the Raman polarizability and well as its real and imaginary parts by noting that

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a,P_a} & = \left[(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a}\right]^S + \left[(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{P_a}\right]^A \\
& = (\alpha_{\alpha\beta})_{g1,g0}^{Q_a} - i\left(\alpha'_{\alpha\beta}\right)_{g1,g0}^{P_a}
\end{aligned} \tag{95}
$$

where in the FFR approximation the separation of the real and imaginary parts of $(\tilde{\alpha}_{\alpha\beta})_{g1,g0}^{Q_a,P_a}$ coincides with separation the symmetric and antisymmetric parts, respectively. The relative magnitudes of these terms is most easily seen from Eq. (92) where the electronic matrix elements and frequency denominators are the same and differences can be expressed within the vibrational matrix elements as

$$\begin{aligned}
&\left\langle\phi^a_{g1}\left|\left(Q_a \pm iP_a/\omega^0_{sg}\right)\right|\phi^a_{g0}\right\rangle\\
&\quad = \left(1 \mp \omega_a/\omega^0_{sg}\right)\left\langle\phi^a_{g1}\left|Q_a\right|\phi^a_{g0}\right\rangle\\
&\left\langle\phi^a_{g1}\left|\left(Q_a \pm iP_a/\omega^0_{se}\right)\right|\phi^a_{g0}\right\rangle\\
&\quad = \left(1 \mp \omega_a/\omega^0_{se}\right)\left\langle\phi^a_{g1}\left|Q_a\right|\phi^a_{g0}\right\rangle
\end{aligned} \tag{96}$$

It can be seen that inclusion of the nuclear velocity dependence of the normal coordinates provides a correction on the order of the ratio of the vibrational energy to that of energy differences between coupled electronic states. This correction is similar in magnitude, but slightly different in form to the correction provided by the NR level of approximation, which depends on the ratio of a vibrational energy to the incident photon energy as shown in Eq. (76). Similar relationships to those in Eqs. (89)–(95) can be written for the Raman optical activity tensors which can be summarized as follows

$$\begin{aligned}
\left(\tilde{G}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0} &= \left(G_{\alpha\beta}\right)^{P_a}_{g1,g0} - i\left(G'_{\alpha\beta}\right)^{Q_a}_{g1,g0} = -\left(\mathscr{G}_{\beta\alpha}\right)^{P_a}_{g1,g0}\\
&\quad + i\left(\mathscr{G}'_{\beta\alpha}\right)^{Q_a}_{g1,g0} = -\left(\tilde{\mathscr{G}}_{\beta\alpha}\right)^{Q_a,P_a}_{g1,g0}
\end{aligned} \tag{97}$$

$$\begin{aligned}
\left(\tilde{A}_{\alpha,\beta\gamma}\right)^{Q_a,P_a}_{g1,g0} &= \left(A_{\alpha,\beta\gamma}\right)^{Q_a}_{g1,g0} - i\left(A'_{\alpha,\beta\gamma}\right)^{P_a}_{g1,g0}\\
&= \left(\mathscr{A}_{\alpha,\beta\gamma}\right)^{Q_a}_{g1,g0} - i\left(\mathscr{A}'_{\alpha,\beta\gamma}\right)^{P_a}_{g1,g0}\\
&= \left(\tilde{\mathscr{A}}_{\alpha,\beta\gamma}\right)^{Q_a,P_a}_{g1,g0}
\end{aligned} \tag{98}$$

and which give rise to the following relationships

$$\begin{aligned}
\left[\left(\tilde{G}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^S &= \frac{1}{2}\left[\left(\tilde{G}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0} + \left(\tilde{G}_{\beta\alpha}\right)^{Q_a,P_a}_{g1,g0}\right]\\
&= -\left[\left(\tilde{\mathscr{G}}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^S
\end{aligned} \tag{99}$$

$$\begin{aligned}
\left[\left(\tilde{G}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^A &= \frac{1}{2}\left[\left(\tilde{G}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0} - \left(\tilde{G}_{\beta\alpha}\right)^{Q_a,P_a}_{g1,g0}\right]\\
&= \left[\left(\tilde{\mathscr{G}}_{\alpha\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^A
\end{aligned} \tag{100}$$

$$\begin{aligned}
\left[\varepsilon_{a\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^S &= \frac{1}{2}\left[\varepsilon_{a\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right.\\
&\quad \left. + \varepsilon_{\beta\gamma\delta}\left(\tilde{A}_{\gamma,\delta\alpha}\right)^{Q_a,P_a}_{g1,g0}\right]\\
&= \left[\varepsilon_{a\gamma\delta}\left(\tilde{\mathscr{A}}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^S
\end{aligned} \tag{101}$$

$$\begin{aligned}
\left[\varepsilon_{a\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^A &= \frac{1}{2}\left[\varepsilon_{a\gamma\delta}\left(\tilde{A}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right.\\
&\quad \left. - \varepsilon_{\beta\gamma\delta}\left(\tilde{A}_{\gamma,\delta\alpha}\right)^{Q_a,P_a}_{g1,g0}\right]\\
&= \left[\varepsilon_{a\gamma\delta}\left(\tilde{\mathscr{A}}_{\gamma,\delta\beta}\right)^{Q_a,P_a}_{g1,g0}\right]^A
\end{aligned} \tag{102}$$

From these last relationships, it can be seen that in the FFR approximation, even though nuclear velocity dependence through P_a leads to antisymmetric contributions to the ordinary Raman polarizability, it does not disturb the relationship between Roman and script forms of the ROA tensor invariants. The antisymmetric ROA invariants are present in the FFR approximation even if only Q_a dependence is retained, but they do not enter any of the expressions for ROA intensity because the anti-symmetric part of Raman polarizability is zero.

9 Imaginary linewidth terms

As a final level of approximation, we consider the effects of the imaginary electronic linewidth terms $i\Gamma_e$ that were last included in Eq. (32). Retaining these terms in the FFR expression in Eq. (33) gives,

$$\begin{aligned}
\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} &= \left\langle\phi^a_{g1}\right| \frac{1}{\hbar}\sum_e \left[\frac{\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg} - (\omega_0 + i\Gamma_e)}\right.\\
&\quad \left. + \frac{\langle g|\hat{\mu}_\beta|e\rangle\langle e|\hat{\mu}_\alpha|g\rangle}{\omega^0_{eg} + (\omega_0 + i\Gamma_e)}\right]\left|\phi^a_{g1}\right\rangle
\end{aligned} \tag{103}$$

where we have grouped the imaginary terms with the incident photon frequency to emphasize that we have merely added imaginary character to the frequency denominator without changing any of the symmetry relations that exist in the FFR theory in Eq. (33). In view of these fundamental symmetry relations, the introduction of imaginary linewidth terms has been expressed in terms of lineshape function f and g, where [3]

$$\begin{aligned}
\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0} &= \mathrm{Re}\left[\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0}\right] + i\,\mathrm{Im}\left[\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0}\right]\\
&= \left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0}(f + ig)
\end{aligned} \tag{104}$$

where we have used the unprimed FFR expression for the Raman tensor $\left(\tilde{\alpha}_{\alpha\beta}\right)^a_{g1,g0}$ and

$$(\tilde{\alpha}_{\alpha\beta})^{a}_{g1,g0}(f) = \frac{2}{\hbar}\left\langle \phi^{a}_{g1}\right| \sum_{e\neq g}\left[\frac{\omega^{0}_{eg}\left[\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}+\Gamma_{e}^{2}\right]\mathrm{Re}\left[\langle g|\hat{\mu}_{\alpha}|e\rangle\langle e|\hat{\mu}_{\beta}|g\rangle_{0}\right]}{\left[\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}+\Gamma_{e}^{2}\right]^{2}+4\omega_{0}^{2}\Gamma_{e}^{2}}\right]\left|\phi^{a}_{g1}\right\rangle \tag{105}$$

$$(\tilde{\alpha}_{\alpha\beta})^{a}_{g1,g0}(g) = \frac{2}{\hbar}\left\langle \phi^{a}_{g1}\right| \sum_{e\neq g}\left[\frac{2\omega^{0}_{eg}\omega_{0}\Gamma_{e}\,\mathrm{Re}\left[\langle g|\hat{\mu}_{\alpha}|e\rangle\langle e|\hat{\mu}_{\beta}|g\rangle_{0}\right]}{\left[\left(\omega^{0}_{eg}\right)^{2}-\omega_{0}^{2}+\Gamma_{e}^{2}\right]^{2}+4\omega_{0}^{2}\Gamma_{e}^{2}}\right]\left|\phi^{a}_{g1}\right\rangle \tag{106}$$

When $\Gamma_e = 0$, Eq. (105) reduces to Eq. (35), Eq. (106) becomes zero, and one has again the FFR theory. The inclusion of lineshape factors does not lead to any change in the number of Raman or ROA invariants, any discrimination in the theory between ICP and SCP ROA, or any intensity predicted for DCP$_{\mathrm{II}}$ ROA.

10 NR Theory with CA and imaginary linewidth contributions

For completeness, we write here the expression of the Raman polarizability with the CA and imaginary lineshape contributions included in the NR theory. Analogous terms can be written for the ROA tensors.

$$\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{Q_a,P_a}_{g1,g0} = \frac{1}{\hbar}\sum_{e\neq g}\Bigg\{ & \sum_{s\neq g}\left(\frac{C^{a}_{sg,0}(\hat{\mu}_{\alpha})_{se,0}(\hat{\mu}_{\beta})_{eg,0}}{\omega^{0}_{eg}-\omega_{0}-i\Gamma_{e}} + \frac{C^{a}_{sg,0}(\hat{\mu}_{\beta})_{se,0}(\hat{\mu}_{\alpha})_{eg,0}}{\omega^{0}_{eg}+\omega_{s}+i\Gamma_{e}}\right) \\
&\times\left\langle\phi^{a}_{g1}\right|\left(Q_a - iP_a/\omega^{0}_{sg}\right)\left|\phi^{a}_{g0}\right\rangle \\
&+\sum_{s\neq e}\left(\frac{(\hat{\mu}_{\alpha})_{gs,0}C^{a}_{se,0}(\hat{\mu}_{\beta})_{eg,0}}{\omega^{0}_{eg}-\omega_{0}-i\Gamma_{e}} + \frac{(\hat{\mu}_{\beta})_{gs,0}C^{a}_{se,0}(\hat{\mu}_{\alpha})_{eg,0}}{\omega^{0}_{eg}+\omega_{s}+i\Gamma_{e}}\right) \\
&\times\left\langle\phi^{a}_{g1}\right|\left(Q_a + iP_a/\omega^{0}_{se}\right)\left|\phi^{a}_{g0}\right\rangle \\
&+\sum_{s\neq e}\left(\frac{(\hat{\mu}_{\alpha})_{ge,0}C^{a}_{se,0}(\hat{\mu}_{\beta})_{sg,0}}{\omega^{0}_{eg}-\omega_{s}-i\Gamma_{e}} + \frac{(\hat{\mu}_{\beta})_{ge,0}C^{a}_{se,0}(\hat{\mu}_{\alpha})_{eg,0}}{\omega^{0}_{eg}+\omega_{0}+i\Gamma_{e}}\right) \\
&\times\left\langle\phi^{a}_{g1}\right|\left(Q_a - iP_a/\omega^{0}_{se}\right)\left|\phi^{a}_{g0}\right\rangle \\
&+\sum_{s\neq e}\left(\frac{(\hat{\mu}_{\alpha})_{ge,0}(\hat{\mu}_{\beta})_{es,0}C^{a}_{sg,0}}{\omega^{0}_{eg}-\omega_{s}-i\Gamma_{e}} + \frac{(\hat{\mu}_{\beta})_{ge,0}(\hat{\mu}_{\alpha})_{es,0}C^{a}_{sg,0}}{\omega^{0}_{eg}+\omega_{0}+i\Gamma_{e}}\right) \\
&\times\left\langle\phi^{a}_{g1}\right|\left(Q_a + iP_a/\omega^{0}_{sg}\right)\left|\phi^{a}_{g0}\right\rangle\Bigg\}
\end{aligned} \tag{107}$$

11 Discussion

Before discussing the NR theoretical formalism, we provide some further comments regarding the scope of the NR theory and rationale for the assumption of equivalence of vibronic structure of the most important excited states compared to that of the ground state. For simplicity, the NR theory in this first presentation is limited to non-generate ground electronic states, an assumption for most molecules lacking a metal coordination center. The simplifying assumption of equivalence of vibrational detail in excited electronic states has been invoked to explain the origin of excitation profiles arising from resonance Raman spectra, as well as the structure fluorescence spectra, in countless publications involving solution-state samples where vibronic detail involves features arising only from the 0–0 and 0–1 interstate vibrational transitions using the same theory presented in this paper.

In the years following the first measurements of SCP ROA [6,24] and DCP$_{\mathrm{I}}$ ROA [8], experiments were carried out to compare the ICP and SCP forms of ROA [16] and the difference between unpolarized ICP and DCP$_{\mathrm{I}}$ ROA in backscattering, thereby isolating for the first time DCP$_{\mathrm{II}}$ ROA [9]. These measurements showed that a chiral molecule devoid of multiple bonds or heteroatoms, such as *cis*- or *trans*-pinane, showed identical ICP and SCP ROA and zero DCP$_{\mathrm{II}}$ ROA to within the noise limit of the measurement. On the other hand, perceptible ICP/SCP ROA differences and non-zero $\mathrm{DCP_{II}}$ ROA of more than several percent in some bands were seen in the sister molecule á-pinene, which has one double bond. Even larger $\mathrm{DCP_{II}}$ ROA spectra were observed in verbenone, which has a conjuagated double bond and carbonyl group, and quinidine, with aromatic character and extensive functional group structure. A correlation between the onset of UV visible absorption and the degree of departure from the FFR approximation was noted, although none of these molecules was in direct resonance with the laser excitation line 514 nm. Clearly, it is possible to see the breakdown of the FFR approximation for a molecule at so-called transparent frequencies with just a single double bond well removed, by more that 25,000 $\mathrm{cm^{-1}}$ from direct resonance. This raises the question, where and by what mechanism does the FFR approximation break down?

In this paper, we describe simple theoretical departures from the standard FFR approximation. The simplest of these is what we call the NR approximation of Raman and ROA intensities. The theory is an intermediate level between the GU theory and the FFR theory. The FFR theory is characterized by use of an adiabatic wavefunction and removal of vibronic detail from the energy denominators of the Raman polarizability and optical activity tensors followed by summation to closure over the excited vibrational state wavefunctions. By contrast, in the NR approximation, the vibronic detail retained using the assumption that the excited vibrational state wavefunctions are the same as those of the ground state and that the summation over the excited vibrational state wavefunctions can be carried out using harmonic oscillator selection rules. The NR expressions for the Raman polarizability and optical activity tensors depend explicitly on both the incident and scattered radiation frequencies. This dual-photon frequency dependence represents the fact that in the NR approximation the molecule has a pre-resonance dependence on both the e0 and e1 vibronic levels the excited electronic states. This dual dependence yields non-zero antisymmetric tensors and invariants for the Raman polarizability and differences between the Roman and script ROA tensors and invariants. As the Raman scattered light approaches Rayleigh scattering in the limit of zero vibrational frequency, the NR theory approaches the FFR theory. By simply changing all scattered frequencies, $\omega_s = \omega_0 - \omega_a$, to the incident laser frequency ω_0 in the NR theory, the FFR theory is obtained; the Raman tensor becomes symmetric; and the distinction between the Roman and script tensors is lost. In the FFR limit, the number of Raman invariants changes from 3 to 2 and the number of ROA invariants changes from 10 and 3, which leads to equality of ICP-ROA and SCP-ROA and zero DCPII-ROA. Even though the NR theory is very simple in form it still retains the same number of Raman and ROA invariant expressions as that found in the full GU theory.

The next simplest departure from the basic FFR theory is to introduce the CA electronic wavefunction that carries nuclear velocity dependence as well as nuclear position dependence. We are able to show that this modification of the FFR theory does not provide a basis for distinguishing the Roman from the script font ROA tensors and invariants, and hence distinguishing ICP and SCP ROA or explaining the observations $\mathrm{DCP_{II}}$ ROA. This extension does, however, lead to antisymmetric components in the Raman tensor and a non-zero antisymmetric invariant. This in turn allows the antisymmetric invariants associated with the magnetic-dipole and electric quadrupole optical activity tensors to contribute to ROA intensities, even though they make no contribution in the FFR approximation. As a result, the number of Raman invariants goes from 2 in the FFR theory to 3 in the CA-FFR theory, but the number of ROA invariant changes only from 3 to 5, rather that the full 3–10 as found in the GU and NR theories of ROA. In the simple FFR theory, without CA contributions, the ROA tensors contain non-zero antisymmetric parts because of the presence of two kinds of operators, in any ROA tensor, but all antisymmetric ROA invariants vanish because each such invariant contains the product of an antisymmetric component of the Raman polarizability tensor with an antisymmetric component of an ROA tensor, and in the FFR approximation, the Raman tensor is pure symmetric.

A third mechanism of departure from the simple FFR theory is to include the imaginary damping terms in the energy denominators. Imaginary contributions are thereby introduced into the FFR polarizability and optical activity tensors, but as shown above, this merely adds lineshape factors to these tensors and does not change their underlying symmetry properties. The imaginary lineshape terms do add accuracy to these tensors as resonance with an excited electronic state is approached, but by their addition is not responsible for any discrimination between ICP and SCP ROA or the appearance of non-zero $\mathrm{DCP_{II}}$ ROA.

It should be clear that all three breakdowns of the FFR, or any combination thereof, can be implemented simultaneously if desired as illustrated in Eq. (107). All three mechanisms carry a similar magnitude of correction to the FFR theory, namely the ratio of a vibrational energy on the order of 1000 $\mathrm{cm^{-1}}$ to the electronic energies or the laser photon energy. It appears however, that the corrections from the CA theory enter with opposing signs for the nuclear velocity dependence and may therefore be diminished in importance relative to corrections from the NR theory.

If one is to explain the appearance of DCP$_{\text{II}}$ ROA at transparent laser frequencies, differences between the Roman and script ROA tensors and invariants must be present in the underlying theory. Before this work, the only option was invoking the full GU theory of ROA. We have demonstrated here that NR theory provides a relatively simple explanation. Further we have ruled out the first order inclusion of nuclear velocity dependence and imaginary linewidth terms as sources of breakdown of the FFR theory of ROA that would lead to differences between the Roman and script ROA tensors, and hence differences between ICP and SCP ROA as well as the appearance of DCP$_{\text{II}}$ ROA.

The NR theory of Raman and ROA is both simple and more accurate than the FFR resonance theory. Even if the vibrational states of the most important low-energy excited electronic state are not that close to those of the ground state, due for example to shallower potential surfaces, shifted equilibrium positions or Dushinsky rotations that mix ground state normal modes, the NR theory is more accurate than the FFR theory since it makes *no attempt* to describe the vibrational structure of the excited electronic states and makes no distinction between the incident and scattered radiation frequencies.

Another hallmark of the superiority of the NR theory over the FFR is that it is straightforward to show that the FFR does not obey time reversal symmetry for ordinary Raman scattering. The time-reversed process of a Stokes Raman scattering event with incident radiation at ω_0 and scattered radiation at $\omega_0 - \omega_a$ is an anti-Stokes Raman scattering event with incident radiation at $\omega_0 - \omega_a$ and scattered radiation at ω_0 . In the FFR approximation, the Raman tensor depends only on ω_0 for the Stokes scattering and only on $\omega_0 - \omega_a$ for the corresponding time-reversed anti-Stokes process and are clearly inequivalent. By contrast in the NR theory, the time-reversed anti-Stokes scattering tensor corresponding to the Stokes tensor in Eq. (73) is

$$\left(\tilde{\alpha}_{\beta\alpha}\right)^{Q_a}_{g1,g0} = \frac{1}{\hbar}\sum_{e\neq g}\left(\frac{\langle g|\hat{\mu}_\beta|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\alpha|g\rangle_0}{\omega^0_{eg}-\omega_s} + \frac{\langle g|\hat{\mu}_\alpha|e\rangle\langle e|\hat{\mu}_\beta|g\rangle_0^{Q_a}}{\omega^0_{eg}+\omega_s} + \frac{\langle g|\hat{\mu}_\beta|e\rangle_0\langle e|\hat{\mu}_\alpha|g\rangle_0^{Q_a}}{\omega^0_{eg}-\omega_0} + \frac{\langle g|\hat{\mu}_\alpha|e\rangle_0^{Q_a}\langle e|\hat{\mu}_\beta|g\rangle_0}{\omega^0_{eg}+\omega_0}\right)\left\langle\phi^a_{g0}\,|Q_a\,\middle|\phi^a_{g1}\right\rangle \qquad (108)$$

where the subscripts α and β corresponding to the scattered and incident light have been interchanged and the initial and final vibrational wavefunctions have been interchanged. Using the Hermitian properties of the electronic and vibrational matrix elements, Eq. (108) can be brought into exact coincidence with Eq. (73) thus proving its time reversal equivalence. This property has been demonstrated previously at the GU level of ROA theory by Barron and Escribano [25] where they also demonstrated similar time-reversal relations between the Roman and script ROA tensors, for example $\left(\tilde{G}_{\alpha\beta}\right)^{Q_a}_{g1,g0} = -\left(\tilde{\mathscr{G}}_{\beta\alpha}\right)^{Q_a}_{g1,g0}$, that also hold exactly in the NR theory. The reason for the equality of Roman and time-reversed script tensors (and *vice versa* for the equality of script and time-reversed Roman tensors) is that the time order of the magnetic-dipole moment interaction relative to electric-dipole moment interaction is reversed as they are in the definitions of the Roman and script tensors. Similarly, the time reversal of an ICP-ROA Stokes process is an SCP-ROA anti-Stokes process.

The time reversal properties of the Raman tensor have been considered previously for both non-resonance [20] and resonance Raman intensities [21]. The formalities of a the time-reversal operator were applied to the Raman tensor to obtain results similar to those obtained here, but in both cases, the time reversal operations focused on the Raman polarizability devoid of explicit excited-state vibronic structure. The treatment of the effects of the breakdown of the Born-Oppenheimer approximation are consistent with our results, as noted above, but the NR theory represents a formulation of the Raman tensor and its breakdown in symmetry not considered previously.

Finally, we address the practical aspect of implementing NR theory as an improvement relative to the FFR theory for quantum mechanical computations of Raman and ROA intensities. Inspection of Eq. (73) shows that the NR theory can be constructed, for a particular scattering frequency from half a FFR calculation at ω_0, namely the two terms involving the derivative with respect to scattered radiation and a second FFR calculation at $\omega_0 - \omega_a$ for the terms involving the derivative of the matrix element involving the incident light. The two terms in Eq. (73) that depend on ω_0 are identical to a standard FFR calculation. If derivatives for the second two terms that depend on $\omega_0 - \omega_a$ are first carried out with respect to Cartesian coordinates one could calculate the results of the FFR theory at several appropriately spaced values of $\omega_0 - \omega_a$ across the Raman spectrum. The variation of these terms with scattering frequency should be smooth, and it is likely that a functional dependence of the desired terms on the frequency of the scattered radiation can be obtained. Interpolated values of the terms could then be used for the transformation to the required Raman or ROA tensor derivatives with respect to a particular normal coordinate for the scattered frequency $\omega_0 - \omega_a$. Numerical studies could then be carried out to find the value of the incident laser frequency, as resonance is approached, where the results of NR theory depart significantly from the FFR theory for pre-resonance Raman and ROA intensities and as a result where ICP ROA becomes distinguishable from SCP ROA, and where DCPII ROA has experimentally observable intensities. One obvious prediction of the NR theory is that these effects will be more noticeable at higher vibrational frequencies than they are at low vibrational frequencies. In other words, the FFR theory should break down and give way to the NR theory first at higher vibrational frequencies.

In looking for the breakdown of the FFR theory, searching for the effects in ROA noted above is much more sensitive that looking for differences in the Raman spectra at two different frequencies for example, because Raman intensities are typically not measured as absolute cross-sections, but more commonly as relative intensities because the varying sensitivities and efficiencies of Raman instruments at different frequencies must be first determined and removed from the measured spectra. However, the breakdown in the FFR can be in observed in ROA at a single laser frequency if for example $\mathrm{DCP_{II}}$ ROA can be measured or if ICP and SCP ROA can be measured for the same sample.

Recently, sum frequency vibrational spectroscopy (SFVS) for chiral liquids has been considered where it is found that the anti-symmetric Raman tensor plays a determining role [26]. Conclusions analogous to those found here are that the contribution of anti-symmetric Raman tensor can be observed well before direct resonance with a single electronic state is encountered. It appears the SFVS and VOA both have sensitivities to the frequency regime between far-from-resonance and strong resonance.

12 Conclusions and summary

A new level of the theory of Raman scattering and ROA is described that lies between the GU and the FFR theories. The NR theory retains some vibronic detail of the excited electronic states of the molecule that is removed in the FFR approximation and is critical to retaining the full richness of the theoretical description of the GU theory of ROA. In particular, the NR theory retains discrimination between the ICP and SCP forms of ROA and non-zero intensities for $\mathrm{DCP_{II}}$ ROA which have been observed experimentally in molecules that are still removed from direct resonance between the laser excitation and excited electronic state. There are various levels of theoretical approximation between the GU theory and the NR theory that correspond to: (1) removal of vibronic detail from the frequency denominators and summation to closure over the excited-state vibrational wavefunctions, (2) removal of imaginary lineshape terms from the frequency denominators of the Raman and ROA tensors, (3) retention of excited-state vibronic sublevels through implementation of the approximations of the NR theory, (4) inclusion of nuclear velocity dependence of the electronic wavefunctions through the use of CA wavefunctions. The first approximation is the most critical in the departure from the GU theory to FFR theory, and at this level it is reasonable not include the imaginary lineshape terms. Approximation 3) yields the NR resonance theory that can be used with or without approximations 1), 2) and 4). The NR theory provides an improved description of the frequency dependence of Raman and ROA intensities in the near-resonance regime as resonance is approached. When resonance with one or two states is approached closely, theoretical descriptions such as the single-electronic-state (SES) theory of ROA or modifications thereof with improved excited-state detail and imaginary lineshape factors will be necessary. The form of the NR theory of Raman and ROA is only slightly more complex than that of the FFR theory and could be implemented for computational analysis to study the relative importance of the various levels of theory described in this paper.

We conclude this section with further considerations on the approximation invoked in the NR theory the vibrational structure of the excited electronic states is the same as ground electronic vibrational structure. The most important point to consider is that for each excited electronic state, a complete sum over all excited state vibrational wavefunctions is performed in the NR approximation. In general, there will be a Dushinsky rotation of the manifold of vibrational normal modes in the exited state relative to the normal modes of the ground state. Both sets of vibrational state wavefunctions span the same Hilbert space as long as the molecule remains intact. Even if the overlap of the nth vibrational state wavefunction in the ground state has a small overlap with the corresponding nth vibrational state wavefunction of the excited state, the sum of all overlaps of the ground vibrational state wavefunction with all excited state vibrational state wavefunctions is still unity, since any particular ground state vibrational wavefunction can be expanded precisely and completely in terms of the set of all vibrational wavefunctions of any particular excited electronic state. If significant overlap with other excited state vibrational wavefunctions occurs, then the error in the NR theory is not one of overlap but of vibrational frequency. The error in the NR approximation is therefore that the frequency for a particular vibronic state used is not that of the corresponding ground state but rather is some average over all the necessary overlaps of excited state wavefunctions. This is not a bad approximation, since the lowest-lying excited states have electronic structures that are relatively mildly distorted compared the ground state and corresponding vibrational modes in the excited state can be recognized relative to the ground state counterparts. Higher excited states with more dramatically distorted electronic structure are suppressed in importance due to their larger energy denominators. On the other hand, the FFR approximation assumes that the frequencies of all the excited-state vibrational modes of the molecule are zero! This is much worse than the simplest attempt to take into account what these effective vibrational frequencies actually are, and in the limit where the value of the vibrational frequency is immaterial compared to the gap between the photon energy and the excited state resonance, the FFR and NR theories become identical. Further, as noted already in the manuscript, the FFR theory does not obey time reversal symmetry, while the NR theory does. The NR theory is the simplest approach to a time-reversal consistent theory.

One might further be concerned that electronic transitions between the ground state and non-bonding orbitals or anti-bonding orbitals would be excluded from an approximation that assumes the vibrational transitions of the excited states are the same as those of the ground state. All that is required in the NR theory is that there is substantial vibrational-state overlap between the ground and excited-state vibrational manifolds. The only transitions that seriously diminish this approximation are transitions that cause dissociation of the molecule into two or more fragments and those high-energy transitions would be reduced in importance by the energy denominator in the expressions for the Raman and ROA tensors. The summation over all excited electronic states is carried out for both the FFR and NR theories of Raman and ROA. Details of the nature the excited vibrational states are not included the final equations of either of these formulations, but the NR theory gives a result that is more realistic and accurate as resonance is approached. Very far from resonance both theories give the same result despite any concerns about the validity of the approximation used to arrive at the NR theory.

References

1. Barron LD, Buckingham AD (1971) Mol Phys 20(6):1111
2. Barron LD, Bogaard MP, Buckingham AD (1973) J Am Chem Soc 95:603
3. Barron LD (2004) Molecular light scattering and optical activity, 2nd edn. Cambridge University Press, Cambridge,
4. Nafie LA (1997) Ann. Rev. Phys. Chem. 48:357
5. Nafie LA, Freedman TB (2000) In: Circular dichroism: principles and applications, 2nd edn. Nakanishi K, Berova N, Woody R (eds) Wiley, New York, pp 97
6. Spencer KM, Freedman TB, Nafie LA (1988) Chem Phys Lett 149:367
7. Nafie LA, Freedman TB (1989) Chem Phys Lett 154:260
8. Che D, Hecht L, Nafie LA (1991) Chem Phys Lett 180:182
9. Yu G-S, Nafie LA (1994) Chem Phys Lett 222:403
10. Hecht L, Nafie LA (1990) Chem Phys Lett 174(6):575
11. Hecht L, Nafie LA (1991) Mol Phys 72:441
12. Nafie LA, Che D (1994) In: Evans M, Kielich S (eds) Modern nonlinear optics, Part 3, vol. 85, Wiley, New York, pp 105
13. Nafie LA (1996) Chem Phys 205:309
14. Polavarapu PL (1990) J Phys Chem 94:8106
15. Ruud K, Helgaker T, Bour P (2002) J Phys Chem A 106:7448
16. Hecht L, Che D, Nafie LA (1992) J Phys Chem 96:4266
17. Buckingham AD, Fischer P (2000) Phys Rev A 61:035801
18. Hassing S, Mortensen OS, Svendsen EN (2000) In: Zhang S-L, Zhu B-F (eds) Proceedings of the 17th conference on Raman spectroscopy. Wiley, Chichester, pp 110
19. Long DA (2002) The Raman Effect. Wiley, Chichester
20. Liu F-C (1991) J Phys Chem 95:7180
21. Liu F-C, Buckingham AD (1993) Chem Phys Lett 207:325
22. Nafie LA (1983) J Chem Phys 79:4950
23. Nafie LA (1992) J Chem Phys 96:5687
24. Hecht L, Che D, Nafie LA (1991) Appl Spectrosc 45:18
25. Barron LD, Escribano JR (1985) Chem Phys 98:437
26. Belkin MA, Shen YR, Harris RA (2004) J Chem Phys 120:10118